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(21) International Application Number: PCT/US98/03592 (22) International Filing Date: 24 February 1998 (24.02.98)			(81) Designated States: CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>																	
(30) Priority Data: <table><tr><td>60/040,754</td><td>13 March 1997 (13.03.97)</td><td>US</td></tr><tr><td>60/044,691</td><td>18 April 1997 (18.04.97)</td><td>US</td></tr><tr><td>60/045,337</td><td>1 May 1997 (01.05.97)</td><td>US</td></tr><tr><td>60/045,357</td><td>2 May 1997 (02.05.97)</td><td>US</td></tr><tr><td>60/045,358</td><td>2 May 1997 (02.05.97)</td><td>US</td></tr><tr><td>60/045,697</td><td>6 May 1997 (06.05.97)</td><td>US</td></tr></table> (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventors: KILLIAN, Christopher, Moore; 1201 Hillendale Road, Gray, TN 37615 (US). MCDEVITT, Jason, Patrick; 3651 Sleepy Hollow Road, Wake Forest, NC 27587 (US). MACKENZIE, Peter, Borden; 1040 Sussex Drive, Kingsport, TN 37660 (US). MOODY, Leslie, Shane; 3322 Pine Timbers Drive, Johnson City, TN 37604 (US). PONASIK, James, Allen, Jr.; 2601 John B. Dennis Highway #1410, Kingsport, TN 37660 (US). (74) Agent: GRAVES, Bernard, J., Jr.; P.O. Box 511, Kingsport, TN 37662-5075 (US).				60/040,754	13 March 1997 (13.03.97)	US	60/044,691	18 April 1997 (18.04.97)	US	60/045,337	1 May 1997 (01.05.97)	US	60/045,357	2 May 1997 (02.05.97)	US	60/045,358	2 May 1997 (02.05.97)	US	60/045,697	6 May 1997 (06.05.97)
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(54) Title: CATALYST COMPOSITIONS FOR THE POLYMERIZATION OF OLEFINS																				
(57) Abstract <p>The present invention includes novel ligands which may be utilized as part of a catalyst system. A catalyst system of the present invention is a transition metal-ligand complex. In particular, the catalyst system includes a transition metal component and a ligand component comprising a Nitrogen atom and/or functional groups comprising a Nitrogen atom, generally in the form of an imine functional group. In certain embodiments, the ligand component may further comprise a phosphorous atom. Preferred ligand components are bidentate (bind to the transition metal at two or more sites) and include a nitrogen-transition metal bond. The transition metal-ligand complex is generally cationic and associated with a weakly coordinating anion. A catalyst system of the present invention may further comprise a Lewis or Bronsted acid. The Lewis or Bronsted acid may be complexed with the ligand component of the transition metal-ligand complex.</p>																				

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TITLE

Catalyst Compositions for the Polymerization of Olefins5 Cross Reference to Related Applications

This application claims the benefit of the following provisional applications under 35 USC § 119: Provisional Application Serial No. 60/040,754, filed March 13, 1997; Provisional Application Serial No. 60/044,691, filed April 18, 1997; Provisional Application Serial No. 10 60/045,337, filed May 1, 1997; Provisional Application Serial No. 60/045,358, filed May 2, 1997; Provisional Application Serial No. 60/045,357, filed May 2, 1997; and Provisional Application Serial No. 60/045,697, filed May 6, 1997.

15 Field of the Invention

The present invention relates to catalyst compositions for olefin polymerization and processes for preparing polyolefins utilizing the catalysts. More particularly, the present invention relates to catalyst compositions comprising ligand complexes comprising nitrogen or nitrogen 20 and phosphorus, for example, phosphine groups, heterocycle groups or imine groups.

Background of the Invention

Olefin polymers are used in a wide variety of products, from 25 sheathing for wire and cable to film. Olefin polymers are used, for instance, in injection or compression molding applications, in extruded films or sheeting, as extrusion coatings on paper, for example photographic paper and digital recording paper, and the like. Improvements in catalysts have made it possible to better control polymerization processes, and, thus, 30 influence the properties of the bulk material. Increasingly, efforts are being made to tune the physical properties of plastics for lightness, strength,

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resistance to corrosion, permeability, optical properties, and the like, for particular uses. Chain length, polymer branching and functionality have a significant impact on the physical properties of the polymer. Accordingly, novel catalysts are constantly sought in attempts to obtain a catalytic process for polymerizing olefins which permits more efficient and better controlled polymerization of olefins.

Conventional polyolefins are prepared by a variety of polymerization techniques, including liquid phase, heterogeneous gas phase, and slurry polymerizations. Certain transition metal catalysts, such as those based on titanium compounds (e.g. TiCl_3 or TiCl_4) in combination with organoaluminum cocatalysts, are used to make linear and linear low density polyethylenes as well as poly- α -olefins such as polypropylene. These so-called "Ziegler-Natta" catalysts are quite sensitive to oxygen and are ineffective for the copolymerization of nonpolar and polar monomers.

Recent advances in non-Ziegler-Natta olefin polymerization catalysis include the following:

L. K. Johnson *et al.*, WO Patent Application 96/23010, discloses the polymerization of olefins using cationic nickel, palladium, iron, and cobalt complexes containing diimine and bisoxazoline ligands. This document also describes the polymerization of ethylene, acyclic olefins, and/or selected cyclic olefins and optionally selected unsaturated acids or esters such as acrylic acid or alkyl acrylates to provide olefin homopolymers or copolymers;

European Patent Application Serial No. 381,495, describes the polymerization of olefins using palladium and nickel catalysts which contain selected bidentate phosphorous containing ligands;

L. K. Johnson *et al.*, *J. Am. Chem. Soc.*, **1995**, *117*, 6414, describes the polymerization of olefins such as ethylene, propylene, and 1-hexene using cationic α -diimine-based nickel and palladium complexes. These catalysts have been described to polymerize ethylene to high molecular

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weight branched polyethylene. In addition, Pd complexes act as catalysts for the polymerization and copolymerization of olefins and methyl acrylate (L. K. Johnson *et al.*, *J. Am. Chem. Soc.*, **1996**, *118*, 267).

5 G.F. Schmidt *et al.*, *J. Am. Chem. Soc.* **1985**, *107*, 1443, describes a cobalt(III) cyclopentadienyl catalytic system having the structure $[\text{C}_5\text{Me}_5(\text{L})\text{CoCH}_2\text{CH}_2-\mu\text{-H}]^+$, which provides for the "living" polymerization of ethylene. In addition, M. Brookhart *et al.*, *Macromolecules* **1995**, *28*, 5378, discloses using such "living" catalysts in the synthesis of end-functionalized polyethylene homopolymers;

10 U. Klabunde, U. S. Patent Nos. 4,906,754; 4,716,205; 5,030,606; 5,175,326; describes the conversion of ethylene to polyethylene using anionic phosphorous/oxygen donors ligated to Ni(II). The polymerization reactions were run between 25 and 100 °C with modest yields, preparing linear polyethylene having a weight-average molecular weight ranging
15 between 8K and 350K. In addition, Klabunde describes the preparation of copolymers of ethylene and functional group containing monomers;

M. Peuckert *et al.*, *Organomet.* **1983**, *2*(5), 594, discloses the oligomerization of ethylene using phosphine/carboxylate donors ligated to Ni(II), which demonstrated modest catalytic activity (0.14 to 1.83 TO/s).
20 The oligomerizations were carried out at 60 to 95 °C and 10 to 80 bar ethylene in toluene, to produce linear α -olefins;

R.E. Murray, U.S. Patents Nos. 4,689,437 and 4,716,138, describes the oligomerization of ethylene using phosphine/sulfonate donors ligated to Ni(II). These complexes show catalyst activities approximately 15 times
25 greater than those reported with phosphine/carboxylate analogs;

W. Keim *et al.*, *Angew. Chem. Int. Ed. Eng.* **1981**, *20*, 116, and V.M. Mohring, *et al.*, *Angew. Chem. Int. Ed. Eng.* **1985**, *24*, 1001, disclose the polymerization of ethylene and the oligomerization of α -olefins with aminobis(imino)phosphorane nickel catalysts; G. Wilke, *Angew. Chem. Int.*

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Ed. Engl. **1988**, 27, 185, describes a nickel allyl phosphine complex for the polymerization of ethylene.

K.A.O. Starzewski *et al.*, *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 63 and U. S. Patent 4,691,036, describes a series of bis(ylide)nickel
5 complexes, used to polymerize ethylene to provide high molecular weight linear polyethylene;

WO Patent Application 97/02298, discloses the polymerization of olefins using a variety of neutral N, O, P, or S donor ligands, in combination with a nickel(0) compound and an acid;

10 Brown *et al.*, WO 97/17380, describes the use of Pd α -diimine catalysts for the polymerization of olefins including ethylene in the presence of air and moisture;

Fink *et al.*, U. S. Patent No. 4,724,273, describes the polymerization of α -olefins using aminobis(imino)phosphorane nickel catalysts and the
15 compositions of the resulting poly(α -olefins);

Additional recent developments are described by Sugimura *et al.*, in JP96-84344, JP96-84343, and WO 9738024, and by Yorisue *et al.*, in JP96-70332

20 Notwithstanding these advances in non-Ziegler-Natta catalysis, there remains a need for efficient and effective Group 8-10 transition metal catalysts for effecting polymerization of olefins. In addition, there is a need for novel methods of polymerizing olefins employing such effective Group 8-10 transition metal catalysts. In particular, there remains a need for Group 8-10 transition metal olefin polymerization catalysts with both improved
25 temperature stability and functional group compatibility. Further, there remains a need for a method of polymerizing olefins utilizing effective Group 8-10 transition metal catalysts in combination with a Lewis acid so as to obtain a catalyst that is more active and more selective.

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Summary of the Invention

The present invention includes novel ligands, which may be utilized as part of a catalyst system. A catalyst system of the present invention is a transition metal - ligand complex. In particular, the catalyst system is
5 comprised of a transition metal component and a ligand component comprising a nitrogen atom, generally in the form of an imine or heterocycle group. In certain embodiments, the ligand component may further comprise a phosphorous atom. Preferred ligand components are bidentate and include a nitrogen - transition metal bond. The transition metal - ligand
10 complex is generally cationic and associated with a weakly coordinating anion.

A catalyst system of the present invention may further comprise a Lewis or Bronsted acid. The Lewis or Bronsted acid may be complexed with the transition metal component and/or the ligand component of the
15 transition metal-ligand complex.

In one aspect of the present invention, the transition metal component of the catalyst system is Group 8-10 transition metals. In another aspect, the catalyst system further comprises a Lewis or Bronsted acid and the transition metal component is Group 8-10 transition metals.
20 Preferred transition metal components include iron (Fe), cobalt (Co), nickel (Ni) and palladium (Pd). The choice of a particular transition metal may be made in view of the end use of the catalyst system.

The present invention also provides processes for preparing polyolefins, preferably having a degree of polymerization of at least 10,
25 comprising contacting one or more monomers, preferably selected from the group comprising $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoralkyl, or R' and R'' collectively form a cyclic olefin, with a catalyst system of the present invention at a temperature and a pressure sufficient to effect polymerization, preferably a temperature of

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-100 to 200 °C, and a pressure of from about 1 atmosphere to 100 atmospheres.

The catalyst system of this invention is extremely versatile in that changes in the ligand or changes to the transition metal itself can be made to obtain a "tailor made" catalyst to suit a particular set of requirements for a particular monomer and polymer. In certain embodiments of the present invention, a Lewis or Bronsted acid may be used as a co-catalyst to render the transition metal more electron deficient, and therefore more active and/or selective, and/or act as a site to bind the catalyst to a surface.

Further features and advantages of the catalyst system and processes of the present invention will become more apparent from the following more detailed description.

Detailed Description of the Invention

The novel ligand components of the present invention are broadly described as comprising a nitrogen atom, preferably in the form of an imine or heterocyclic functional group.

A catalyst system of the present invention may further comprise a Lewis or Bronsted acid, which may be complexed with the ligand component or the transition metal component. While not wishing to be bound by theory, it is believed that the Lewis acid complexation can render the transition metal more electron deficient, and therefore more active and/or selective, and/or act as a site to bind the catalyst to a surface. Although this strategy may be implemented in a variety of ways, ligands in which the Lewis acid is bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to the transition metal are preferred.

In one aspect of the present invention, the transition metal component of the catalyst system is a Group 8-10 transition metal. In another aspect, the catalyst system further is a Lewis or Bronsted acid and

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the transition metal component is a Group 8-10 transition metal. A catalyst system of the present invention may advantageously be utilized in a process for the polymerization of olefins, including ethylene and α -olefins such as propylene and 1-hexene and cyclic olefins such as cyclopentene and norbornene. Accordingly, a process of the present invention is contacting one or more monomers comprising $R'CH=CHR''$ with a catalyst system of the present invention at a temperature and a pressure sufficient to effect polymerization, preferably a temperature of -100 to 200 $^{\circ}C$, more preferably a temperature from 25 to 150 $^{\circ}C$, and a pressure of from about 1 atmosphere to 100 atmospheres, wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin. The possible embodiments of a process of the present invention for the production of polyolefins include processes utilizing the catalyst systems of the present invention described herein.

The embodiments of a catalyst system of the present invention are described in detail below utilizing the following terms defined as follows:

Symbols ordinarily used to denote elements in the Periodic Table take their ordinary meaning, unless otherwise specified. Thus, N, O, S, P, and Si stand for nitrogen, oxygen, sulfur, phosphorus and silicon, respectively.

Examples of neutral Lewis bases include, but are not limited to, ethers, organic nitriles or organic sulfides.

Examples of Lewis acids include, but are not limited to, methylalumoxane (hereinafter MAO) and other aluminum sesquioxides, R^7_3Al , R^7_2AlCl , R^7AlCl_2 (where R^7 is alkyl), organoboron compounds, boron halides, $B(C_6F_5)_3$, $R^9_3Sn[BF_4]$, (where R^9 is alkyl or aryl), $MgCl_2$, and H^+X^- , where X^- is a weakly coordinating anion.

A "hydrocarbyl" group means a monovalent or divalent, linear, branched or cyclic group which contains only carbon and hydrogen atoms. Examples of monovalent hydrocarbyls include the following: C_1 - C_{20} alkyl;

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C₁-C₂₀ alkyl substituted with one or more groups selected from C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl or aryl; C₃-C₈ cycloalkyl; C₃-C₈ cycloalkyl substituted with one or more groups selected from C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl or aryl; C₆-C₁₄ aryl; and C₆-C₁₄ aryl substituted with one or more groups selected from C₁-C₂₀ alkyl, C₃-C₈ cycloalkyl or aryl. As used herein, the term "aryl" preferably denotes a phenyl, naphthyl, or anthracenyl group. When the above groups are substituted, they are preferably substituted from one to four times with the listed groups. Examples of divalent (bridging hydrocarbyls) include: -CH₂-, -CH₂CH₂-, -C₆H₄-, and -CH₂CH₂CH₂-.

Specific examples of the group G as used herein include but are not limited to: -CH₂-CH₂-, -CH=CH-, -CH₂-, and -C₆H₄-. Specific examples of G¹ as used herein include, but are not limited to: -CH₂-CH₂-CH₂-, -CH₂-CH₂-CH₂-CH₂-, -O-CH₂-C(CH₃)₂-, -S-CH=CH-, -S-CH₂-CH₂-, -O-CH=CH-, -N=CH-CH=CH-, -CH=CH-CH=CH-, -CH=N-CH=CH-, -NPh-CH=CH-, and -N(CH₃)-C₆H₄-. Specific examples of G² as used herein include, but are not limited to: -CH₂-CH₂-, -CH₂-O-, -N(CH₃)-CH₂-, -CH₂-CH₂-O-, -N(CH₃)-CH₂-CH₂-, -S-CH₂-, -S-CH₂-CH₂-, -CH=CH-, -CH=N-, -CH=CH-CH₂-, -CH=N-CH₂-, and -C₆H₄-.

A "silyl" group refers to a SiR₃ group where Si is silicon and R is hydrocarbyl or substituted hydrocarbyl or silyl, as in Si(SiR₃)₃.

A "heteroatom" refers to an atom other than carbon or hydrogen. Preferred heteroatoms include oxygen, nitrogen, phosphorus, sulfur, selenium, arsenic, chlorine, bromine, and fluorine.

The term "fluoroalkyl" as used herein refers to a C₁-C₂₀ alkyl group substituted with one or more fluorine atoms.

A "substituted hydrocarbyl" refers to a monovalent or divalent hydrocarbyl substituted with one or more heteroatoms. Examples of monovalent substituted hydrocarbyls include: trifluoromethyl, 2,6-dimethyl-4-methoxyphenyl, 2,6-diisopropyl-4-methoxyphenyl, 4-cyano-2,6-

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dimethylphenyl, 2,6-dimethyl-4-nitrophenyl, 2,6-difluorophenyl, 2,6-dibromophenyl, 2,6-dichlorophenyl, 4-methoxycarbonyl-2,6-dimethylphenyl, 2-tert-butyl-6-chlorophenyl, 2,6-dimethyl-4-phenylsulfonylphenyl, 2,6-dimethyl-4-trifluoromethylphenyl, 2,6-dimethyl-4-trimethylammoniumphenyl
5 (associated with a weakly coordinating anion), 2,6-dimethyl-4-hydroxyphenyl, 9-hydroxyanthr-10-yl, 2-chloronaph-1-yl, 4-methoxyphenyl, 4-nitrophenyl, and 9-nitroanthr-10-yl. Examples of divalent substituted hydrocarbyl include: 4-methoxy-1,2-phenylene, 1-methoxymethyl-1,2-ethanediyl, 1,2-bis(benzyloxymethyl)-1,2-ethanediyl, and 1-(4-methoxyphenyl)-1,2-ethanediyl.
10

A "mono-olefin" means a hydrocarbyl group having one carbon-carbon double bond.

A "suitable nickel precursor" refers to a nickel compound which may be combined with compound III, VI, IX, or XII, and optionally a Lewis or
15 Bronsted acid, to form an active olefin polymerization catalyst. Examples include: bis(1,5-cyclooctadiene)nickel(0), (1,2-dimethoxyethane)nickel(II) dibromide, bis[(chloro)(1, 2, 3- η^3 -2-propenyl) nickel(II)].

The term "polymer" as used herein is meant a species comprised of monomer units and having a degree of polymerization (DP) of ten or higher.

20 The term "weakly coordinating counterion" is well-known in the art *per se* and generally refers to a large bulky anion capable of delocalization of the negative charge of the anion. Suitable weakly coordinating anions include, but are not limited to, PF_6^- , BF_4^- , SbF_6^- , $(\text{Ph})_4\text{B}^-$ where Ph = phenyl, BAR_4 where BAR_4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. The
25 coordinating ability of such anions is known and described in the literature (Strauss, S. *et al.*, *Chem. Rev.* **1993**, 93, 927).

As used herein, the terms "monomer" or "olefin monomer" refer to the olefin or other monomer compound before it has been polymerized. The term "monomer units" refers to the moieties of a polymer that
30 correspond to the monomers after they have been polymerized;

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In some cases, a compound Y is required as a cocatalyst. Suitable compounds Y include a neutral Lewis acid capable of abstracting Q⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion. Preferred compounds Y include:

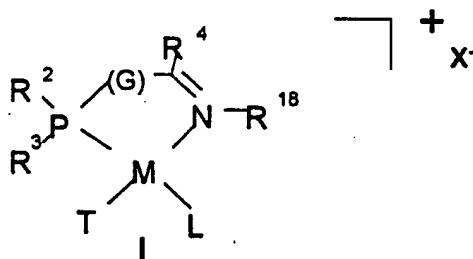
5 methylalumoxane (hereinafter MAO) and other aluminum sesquioxides, R⁷₃Al, R⁷₂AlCl, R⁷AlCl₂ (where R⁷ is alkyl), organoboron compounds, boron halides, B(C₆F₅)₃, R⁹₃Sn[BF₄], (where R⁹ is alkyl or aryl), MgCl₂, and H⁺X⁻, where X⁻ is a weakly coordinating anion.

10 Especially preferred olefin monomers include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, cyclopentene, and norbornene.

First Embodiment of the Present Invention

In a first embodiment, the present invention provides a catalyst system comprising: an imine/phosphine ligand. In a first aspect, the catalyst system is a compound of the formula I:

15



20 wherein:

R² and R³ are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R² and R³ may be taken together with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

25 R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R¹⁸ is hydrocarbyl or substituted hydrocarbyl;

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T is hydrogen or hydrocarbyl group;

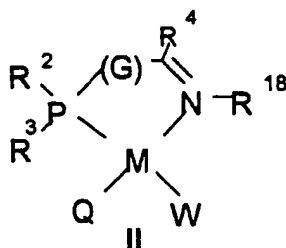
L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen, or sulfur;

M is Ni(II), Pd(II), or Co(II); and

5 X is a weakly coordinating anion.

In a second aspect, this first embodiment of the present invention provides a catalyst system formed by contacting a first compound Y with a second compound II having the formula:

10



wherein:

15 R² and R³ are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R² and R³ may be taken together with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl and may comprise a cyclic olefin;

20 R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R¹⁸ is hydrocarbyl or substituted hydrocarbyl;

Q is hydrocarbyl, chloride, iodide or bromide;

W is hydrocarbyl, chloride, iodide or bromide;

M is Ni(II), Pd(II), or Co(II);

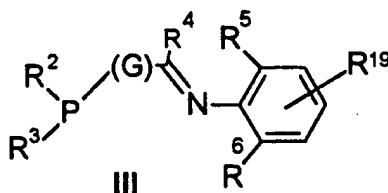
25 and Y is selected from a neutral Lewis acid capable of abstracting Q⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion

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is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

Preferred neutral Lewis acids include: MAO and other aluminum sesquioxides, R_3^7Al , R^7_2AlCl , R^7AlCl_2 where R^7 is alkyl. Complex II and compound Y may be combined in the liquid phase. The liquid phase may include solvent or neat monomer. In a process for preparing polyolefins, complex II and compound Y may be combined in the presence of monomer. The molar ratio of compound Y to complex II may be from about 10 to 10,000.

In a third aspect, the first embodiment of the present invention provides a compound III of the formula:



wherein

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

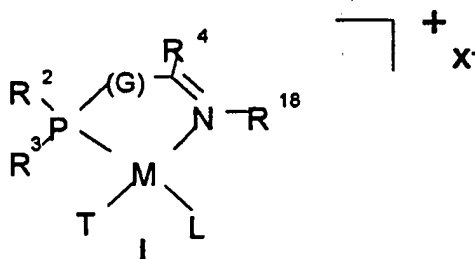
R^{19} is hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, or nitro;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^5 and R^6 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl or a halide; provided that R^5 and R^6 are not both hydrogen.

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The present invention also provides a process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin;
 5 with a catalyst comprising a compound of formula I:



wherein:

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together
 10 with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^{18} is hydrocarbyl or substituted hydrocarbyl;

T is hydrogen or hydrocarbyl;

15 L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen, or sulfur;

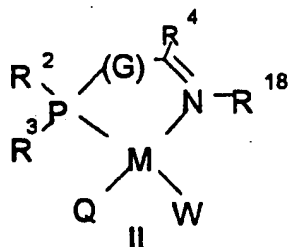
M is Ni(II), Pd(II), or Co(II); and

X^- is a weakly coordinating anion;

at a temperature and a pressure sufficient to effect polymerization.

20 In a further preferred embodiment, there is provided a process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin;
 with a catalyst system wherein the catalyst is formed by contacting a first
 25 compound Y with a second compound II having the formula:

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wherein:

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^{18} is hydrocarbyl or substituted hydrocarbyl;

Q is hydrocarbyl, chloride, iodide or bromide;

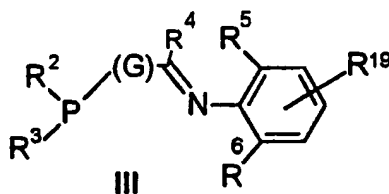
W is hydrocarbyl, chloride, iodide or bromide;

M is Ni(II), Pd(II), or Co(II);

and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion at a temperature and a pressure sufficient to effect polymerization.

In a further preferred embodiment, there is provided a process for the polymerization of olefins comprising contacting a compound of the formula III with a suitable nickel precursor and one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin:

- 15 -



wherein

5 R² and R³ are each independently selected from hydrocarbyl or substituted hydrocarbyl, or R² and R³ may be taken together with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl and may comprise a cyclic olefin;

10 R¹⁹ is hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, or nitro;

R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl; and

15 R⁵ and R⁶ are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl or halide; provided that R⁵ and R⁶ are not both hydrogen.

Compound III may be utilized as a precursor to complex I or II.

Complexes I and II, may be synthesized by a method analogous to that described in the literature (Johnson *et al.*, *J. Am. Chem. Soc.* **1995**, *117*, 6414).

20 The skilled artisan, in possession of this disclosure, could make the present compounds without undue experimentation. Methods of synthesizing complexes I, II, and compound III, are also illustrated in the following examples.

25 Preferred ligand components for use in complex I or II and preferred catalyst systems utilizing complex I or II are also set forth in the following examples.

- 16 -

Preferred polyolefin products will have a degree of polymerization of at least 10. A preferred olefin monomer is $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin. The preferred temperature range of about
5 -100 to 200 °C, more preferably a temperature from about 25 to 150 °C; a preferred pressure is about 1 atmosphere to 100 atmospheres.

Examples of processes for preparing polyolefins utilizing complex I or complex II of the first embodiment of the present invention are set forth in the following examples.

10

Second-Fourth Embodiments of the Present Invention

The second, third, and fourth embodiments of the present invention provide catalyst systems comprising transition metal-ligand complexes wherein the ligand component is a bidentate ligand which binds to a
15 transition metal and is a heterocycle and an additional nitrogen donor group such as an imine or imidate ester.

Second Embodiment of the Present Invention

The second embodiment of the present invention provides a catalyst
20 system comprising a transition metal complex of bidentate ligands (imino-substituted heterocycles) having a five-membered ring, formed by the metal complex, and comprising one metal atom, one carbon atom, and three nitrogen atoms.

The olefin polymerization catalysts of the second embodiment of the
25 present invention comprise transition metal complexes of bidentate ligands that can be referred to as imino-substituted heterocycles, more specifically imino-substituted pyrazoles and other related heterocycles with adjacent 1,2-nitrogen atoms. The transition metal component is a Group 8-10 transition metal. Nickel, cobalt and palladium are preferred transition
30 metals. The ligands may also be referred to using a "imine/heterocycle" or

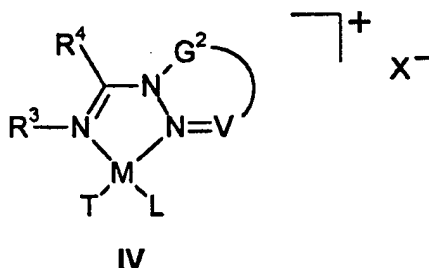
- 17 -

"heterocycle/ imine" nomenclature which describes the two components of the bidentate ligand, e.g., imine/triazole. The five-membered ring formed by the transition metal complex contains one transition metal atom, one carbon atom, and three nitrogen atoms (two of which are provided by the

5 heterocycle component of the bidentate ligand).

In a first aspect the second embodiment of the present invention provides a catalyst system comprising a transition metal-ligand complex of the formula IV:

10



15 wherein:

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-

20 membered heterocyclic ring comprising G^2 , V, N, and N;

V is CR^6 , N, or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with

25 phosphorus;

T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

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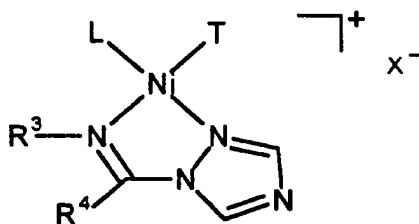
L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen, sulfur;

M is Ni(II), Pd(II), or Co(II); and

X⁻ is a weakly coordinating anion.

5

A preferred embodiment of the present invention involves a catalyst of the formula XVI:



10

wherein:

R³ is hydrocarbyl or substituted hydrocarbyl;

R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

15

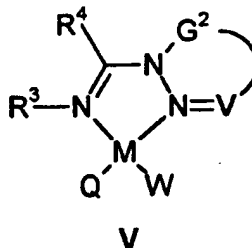
L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur; and

X⁻ is a weakly coordinating anion.

20

In a second aspect, this second embodiment of the present invention provides a catalyst system formed by contacting a first compound Y with a second compound V having the formula:

- 19 -



wherein:

- 5 R^3 is hydrocarbyl or substituted hydrocarbyl;
 R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;
 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a
 carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-
 membered heterocyclic ring comprising G^2 , V, N, and N;
 10 V is CR^6 , N, or PR^6R^9 ;
 R^6 and R^9 are each independently selected from hydrogen,
 hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected
 hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with
 phosphorus;
 15 Q is hydrocarbyl, chloride, iodide, or bromide;
 W is hydrocarbyl, chloride, iodide, or bromide;
 M is Ni(II), Pd(II), or Co(II);
 and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^-
 to form a weakly coordinating anion, a cationic Lewis acid whose counterion
 20 is a weakly coordinating anion, or a Bronsted acid whose conjugate base is
 a weakly coordinating anion.

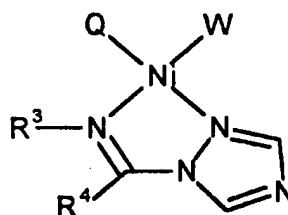
Preferred neutral Lewis acids include: MAO and other aluminum
 sesquioxides, R_3^7Al , R^7_2AlCl , and R^7AlCl_2 wherein R^7 is alkyl. Complex V
 25 and compound Y may be combined in the liquid phase. The liquid phase

- 20 -

may include solvent or neat monomer. In a process for preparing polyolefins, complex V and compound Y may be combined in the presence of monomer. The molar ratio of compound Y to complex V may be from about 10 to 10,000.

5

A preferred embodiment of the present invention involves a catalyst of the formula XVII:



XVII

10

wherein:

R³ is hydrocarbyl or substituted hydrocarbyl;

R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

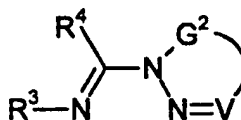
15

Q is a hydrocarbyl, chloride, iodide, or bromide; and

W is a hydrocarbyl, chloride, iodide, or bromide.

In a third aspect, the second embodiment of present invention provides a compound VI of the formula:

20



VI

- 21 -

wherein:

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

5 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

V is CR^6 , N, or PR^6R^9 ;

10 R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

Compound VI may be utilized as a precursor to complex IV or V.

15 Complexes IV and V may be synthesized by a method analogous to that described in the literature (Johnson *et al.*, *J. Am. Chem. Soc.* **1995**, *117*, 6414).

20 The skilled artisan, in possession of this disclosure, could make the present compounds without undue experimentation. Methods of synthesizing complexes IV and V, and compound VI are also illustrated in the following examples.

Preferred ligand components for use in complex IV or V and preferred catalyst systems utilizing complex IV or V are also set forth in the following examples.

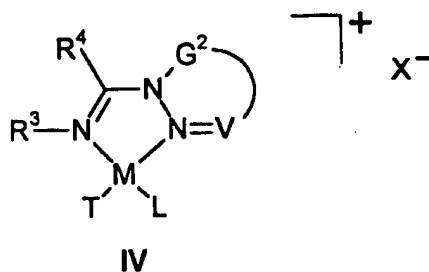
25 The present invention also provides processes for preparing polyolefins utilizing complexes IV, V, and compound VI.

Thus, the present invention provides a process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen,

- 22 -

hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin;
with the a catalyst comprising a compound of formula IV:

5



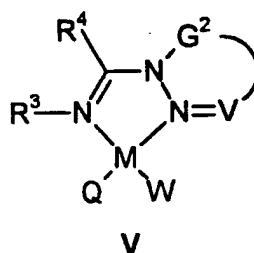
wherein:

- 10 R³ is hydrocarbyl or substituted hydrocarbyl;
 R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;
 G² is hydrocarbyl or substituted hydrocarbyl and may comprise a
 carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-
 membered heterocyclic ring comprising G², V, N, and N;
- 15 V is CR⁶, N, or PR⁶R⁹;
 R⁶ and R⁹ are each independently selected from hydrogen,
 hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected
 hydrocarbyl, and in addition, R⁶ and R⁹ may collectively form a ring with
 phosphorus;
- 20 T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;
 L is a monoolefin or a neutral Lewis base where the donating
 atom is nitrogen, oxygen or sulfur;
 M is Ni(II), Pd(II), or Co(II); and X⁻ is a weakly coordinating anion;
 at a temperature and a pressure sufficient to effect polymerization.
- 25 Accordingly, the invention also provides a process for preparing
 polyolefins comprising contacting one or more olefin monomers of the

- 23 -

formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst wherein the catalyst is formed by contacting a first compound Y with a second compound V having the formula:

5



wherein:

10

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

15

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

V is CR^6 , N, or PR^6R^9 ;

20

R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

Q is hydrocarbyl, chloride, iodide, or bromide;

W is hydrocarbyl, chloride, iodide, or bromide;

M is Ni(II), Pd(II), or Co(II);

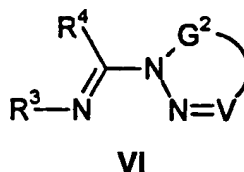
25

and Y is a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a

- 24 -

weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion; at a temperature and a pressure sufficient to effect polymerization.

The invention also provides a process for the polymerization of olefins comprising contacting a compound of the formula VI with a suitable nickel precursor, optionally a Bronsted or Lewis acid and one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin:



wherein:

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

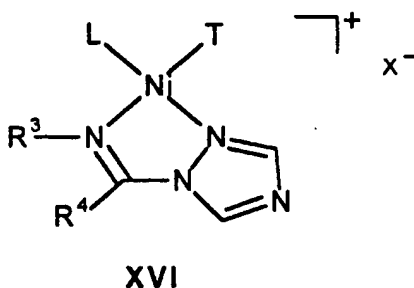
V is CR^6 , N, or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus.

The invention also provides processes for preparing polyolefins utilizing the compounds of formula XVI and XVII.

- 25 -

Thus, the present invention provides a process for preparing polyolefins comprising contacting one or more olefin monomers having the composition $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin;
 5 with a catalyst comprising the formula **XVI**:



wherein:

10

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

15

L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur; and

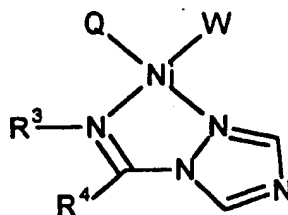
X^- is a weakly coordinating anion at a temperature and a pressure sufficient to effect polymerization.

20

Accordingly, the invention also provides a process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with the catalyst system comprising a compound of the formula **XVII** and a second compound Y:

25

- 26 -



XVII

wherein:

- 5 R³ is hydrocarbyl or substituted hydrocarbyl;
 R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;
 Q is hydrocarbyl, chloride, iodide, or bromide; and
 W is hydrocarbyl, chloride, iodide, or bromide;

and Y is a neutral Lewis acid capable of abstracting Q⁻ or W⁻ to form a
 10 weakly coordinating anion, a cationic Lewis acid whose counterion is a
 weakly coordinating anion, or a Bronsted acid whose conjugate base is a
 weakly coordinating anion; at a temperature and a pressure sufficient to
 effect polymerization.

Preferred polyolefin products will have a degree of polymerization
 15 (DP) of at least 10. A preferred olefin monomer is R'CH=CHR'' wherein R'
 and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R''
 may be linked to form a cyclic olefin. Preferred temperature conditions are
 -100 to 200 °C. Preferred pressure conditions are from about 1
 atmosphere to 100 atmospheres.

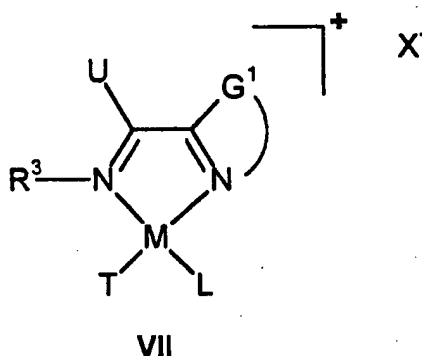
20 Examples of processes for preparing polyolefins utilizing complex IV
 or V of the second embodiment of the present invention are set forth in the
 following examples.

Third Embodiment of the Present Invention

- 27 -

The third embodiment of the present invention provides a class of olefin polymerization catalysts based on late transition metal complexes of bidentate ligands comprising one imidate ester, thioimide ester, selenoimide ester, or amidine N-donor fragment, and one heterocyclic N-donor fragment, the two fragments together comprising a neutral bidentate, N,N-donor ligand. In one aspect, the catalyst "system" further comprises a Lewis or Bronsted acid.

In a first aspect, the third embodiment of the present invention provides a catalyst system comprising a transition metal-ligand complex of the formula VII:



wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1 , C, and N;

T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

- 28 -

L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur;

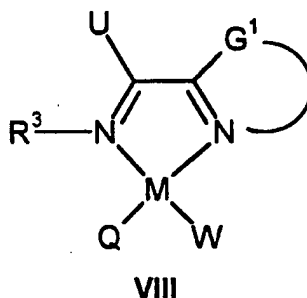
M is Ni(II), Pd(II), or Co(II); and

X⁻ is a weakly coordinating anion.

5

In a second aspect this third embodiment of the present invention provides a catalyst system formed by contacting a first compound Y with a second compound VIII having the formula:

10



wherein:

R³ is hydrocarbyl, substituted hydrocarbyl or silyl;

15 U is OR⁴, SR⁴, SeR⁴ or NR⁴R⁸;

R⁴ and R⁸ are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R⁴ and R⁸ may collectively form a ring with nitrogen;

20 G¹ is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G¹, C, and N;

M is Ni(II), Pd(II), or Co(II);

Q is hydrocarbyl, chloride, iodide, or bromide;

W is hydrocarbyl, chloride, iodide, or bromide;

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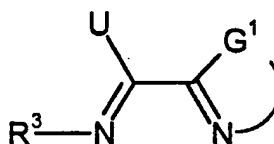
and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

5

Preferred neutral Lewis acids include: MAO and other aluminum sesquioxides, R_3^7Al , R^7_2AlCl , and R^7AlCl_2 wherein R^7 is alkyl. Complex VIII and compound Y may be combined in the liquid phase. The liquid phase may include solvent or neat monomer. In a process for preparing polyolefins, complex VIII and compound Y may be combined in the presence of monomer. The molar ratio of compound Y to complex VIII may be from about 10 to 10,000.

10

In a third aspect, the third embodiment of the present invention provides a compound IX of the formula:



IX

15

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

20

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen; and

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1 , C, and N.

25

- 30 -

Compound IX may be utilized as a precursor to complex VII or VIII.

Complexes VII and VIII may be synthesized by a method analogous to that described in the literature (Johnson *et al.*, *J. Am. Chem. Soc.* **1995**, *117*, 6414).

5 The skilled artisan, in possession of this disclosure, could make the present compounds without undue experimentation. Methods of synthesizing complexes VII and VIII, and compounds IX, are also illustrated in the following examples.

10 Preferred ligand components for use in complex VII or VIII and preferred catalyst systems utilizing complex VII or VIII are also set forth in the following examples.

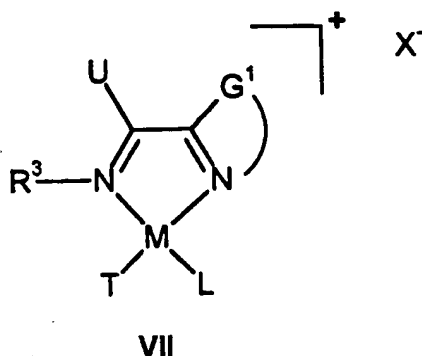
The present invention also provides processes for preparing polyolefins utilizing complexes VII, VIII, and compound IX.

15 Thus, the present invention provides a process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst comprising a compound of the formula VII:

20

25

- 31 -



5

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

10

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

15

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1 , C, and N;

T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur;

M is Ni(II), Pd(II), or Co(II); and

20

X^- is a weakly coordinating anion; at a temperature and a pressure sufficient to effect polymerization.

The invention also provides a process for preparing polyolefins comprising contacting one or more olefin monomers of the formula

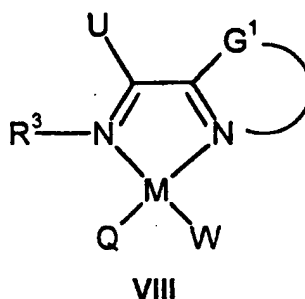
$R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl,

25

fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst

- 32 -

system wherein the catalyst is formed by contacting a first compound Y with a second compound VIII having the formula:



5

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

10

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1 , C, and N;

15

M is Ni(II), Pd(II), or Co(II);

Q is an hydrocarbyl, chloride, iodide, or bromide;

W is hydrocarbyl, chloride, iodide, or bromide;

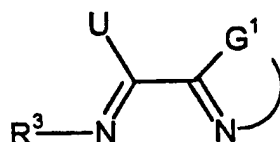
and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^-

20

to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion; at a temperature and a pressure sufficient to effect polymerization.

- 33 -

The invention also provides a process for the polymerization of olefins comprising contacting a compound of the formula IX with a suitable nickel precursor, optionally a Lewis or Bronsted acid and one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin:



IX

10

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

15

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1 , C, and N.

20

Preferred polyolefin products will have a degree of polymerization (DP) of at least 10. A preferred olefin monomer is $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin. Preferred temperature conditions are -100 to 200 °C. Preferred pressure conditions are from about 1 atmosphere to 100 atmospheres.

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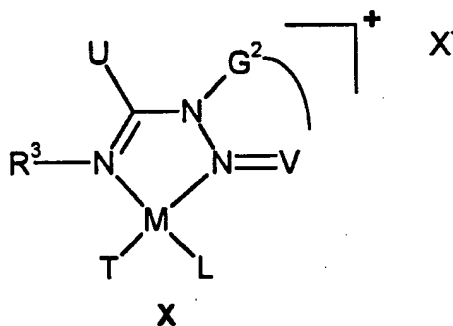
Examples of processes for preparing polyolefins utilizing VII or VIII of the third embodiment of the present invention are set forth in the following examples.

5 Fourth Embodiment of the Present Invention

The fourth embodiment of the present invention also provides a class of olefin polymerization catalysts based on Group 8-10 transition metal complexes of bidentate ligands comprising one imidate ester, thioimide ester, selenoimide ester, or amidine N-donor fragment, and one
 10 heterocyclic N-donor fragment, the two fragments together comprising a neutral bidentate, N,N-donor ligand. In one aspect, the catalyst "system" further comprises a Lewis or Bronsted acid.

In a first aspect, the fourth embodiment of the present invention provides a catalyst system comprising a compound of the formula X:

15



wherein:

- 20 R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;
 U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;
 R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;
 25 V is CR^6 , N , or PR^6R^9 ;

- 35 -

R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

5 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

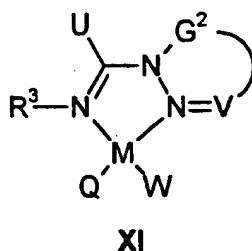
T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

10 L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur;

M is Ni(II), Pd(II) or Co(II); and

X^- is a weakly coordinating anion.

15 In a second aspect, this fourth embodiment of the present invention provides a catalyst system formed by contacting a first compound Y with a second compound XI having the formula:



20

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

25 R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

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V is CR⁶, N, or PR⁶R⁹;

R⁶ and R⁹ are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R⁶ and R⁹ may collectively form a ring with
5 phosphorus;

G² is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G², V, N, and N;

M is Ni(II), Pd(II), or Co(II);

10 Q is hydrocarbyl, chloride, iodide, or bromide;

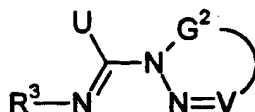
W is hydrocarbyl, chloride, iodide, or bromide;

and Y is selected from a neutral Lewis acid capable of abstracting Q⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is
15 a weakly coordinating anion.

Preferred neutral Lewis acids include: MAO and other aluminum sesquioxides, R₃⁷Al, R⁷₂AlCl, R⁷AlCl₂ where R⁷ is alkyl. Complex XI and compound Y may be combined in the liquid phase. The liquid phase may include solvent or neat monomer. In a process for preparing polyolefins,
20 complex XI and compound Y may be combined in the presence of monomer. The molar ratio of compound Y to complex XI may be from about 10 to 10,000.

In a third aspect, the fourth embodiment of the present invention
25 provides a compound XII of the formula:

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XII

5 wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen,
hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may
10 collectively form a ring with nitrogen;

V is CR^6 , N, or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen,
hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected
hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with
15 phosphorus;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a
carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-
membered heterocyclic ring comprising G^2 , V, N, and N.

Compound XII may be utilized as a precursor to complex X or XI.

20 Complexes X and XI may be synthesized by a method analogous to
that described in the literature (Johnson *et al.*, *J. Am. Chem. Soc.* **1995**,
117, 6414).

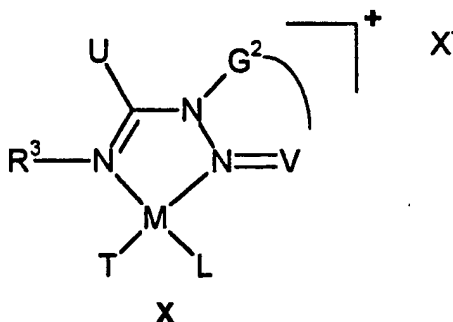
The skilled artisan, in possession of this disclosure, could make the
present compounds without undue experimentation. Methods of
25 synthesizing complexes X and XI, and compounds XII, are also illustrated in
the following examples.

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Preferred ligand components for use in complex **X** or **XI** and preferred catalyst systems utilizing complex **X** or **XI** are also set forth in the following examples.

The present invention also provides processes for preparing
 5 polyolefins utilizing the complexes **X**, **XI**, and compound **XII**.

Thus, the present invention provides a process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin;
 10 with a composition catalyst comprising the formula **X**:



15

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

20 R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

V is CR^6 , N, or PR^6R^9 ;

25 R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected

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hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

T is hydrogen, hydrocarbyl, or a substituted hydrocarbyl;

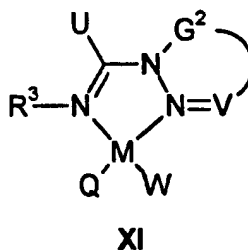
L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen, sulfur;

M is Ni(II), Pd(II), or Co(II); and

X^- is a weakly coordinating anion;

at a temperature and a pressure sufficient to effect polymerization.

The invention also provides a process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst system wherein the catalyst is formed by contacting a first compound Y with a second compound XI having the formula:



25 wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

- 40 -

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

5 V is CR^6 , N, or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

10 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

M is Ni(II), Pd(II), or Co(II);

Q is hydrocarbyl, chloride, iodide, or bromide;

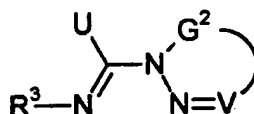
15 W is hydrocarbyl, chloride, iodide, or bromide;

and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion;

20 at a temperature and a pressure sufficient to effect polymerization.

The invention also provides a process for the polymerization of olefins comprising contacting a compound of the formula XII with a suitable nickel precursor, optionally a Lewis or Bronsted acid and one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently
25 hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin:

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XII

5 wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen,
hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may
10 collectively form a ring with nitrogen;

V is CR^6 , N, or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen,
hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected
hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with
15 phosphorus;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a
carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-
membered heterocyclic ring comprising G^2 , V, N, and N.

Preferred polyolefin products will have a degree of polymerization
20 (DP) of at least 10. A preferred olefin monomer is $R'CH=CHR''$ wherein R'
and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R''
may be linked to form a cyclic olefin. Preferred temperature conditions are
-100 to 200 °C. Preferred pressure conditions are from about 1
atmosphere to 100 atmospheres.

25 Examples of processes for preparing polyolefins utilizing complex X
or complex XI of the fourth embodiment of the present invention are set
forth in the following examples.

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Fifth Embodiment of the Present Invention

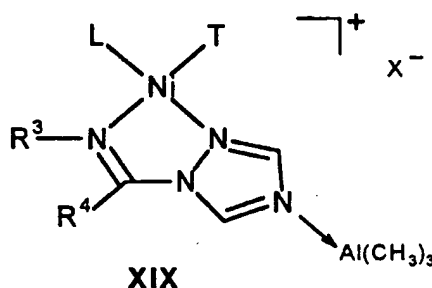
In a fifth embodiment, the present invention provides a catalyst system comprising a transition metal - ligand complex further complexed with one or more Lewis acids to obtain an active olefin polymerization catalyst. Suitable ligands for use in the transition metal-ligand complex comprise the ligand components described above with reference to the second, third and fourth embodiments of the present invention. A preferred transition metal is nickel.

Examples include methylaluminoxane, alkylaluminums, alkylaluminum halides, organoboron compounds, boron halides, $B(C_6F_5)_3$, $Li[BF_4]$, $R_3Sn[BF_4]$, $MgCl_2$, $M_3SiCl/SnCl_4$, $SbCl_5$, alumina H^+X^- , where X^- is a relatively non-coordinating anion, and Montmorillonite clay.

An electron deficient metal center is advantageous for efficient olefin polymerization. The fifth embodiment of the present invention provides catalyst systems wherein a binucleating or multinucleating ligand is complexed to a transition metal and one or more Lewis acids to obtain an active olefin polymerization catalyst. While not wishing to be bound by any theory, it is believed that the Lewis acid complexation renders the transition metal more electron deficient rendering the transition metal more active and/or selective, and/or available as a site to bind the catalyst system to a surface. Thus, broadly, catalyst systems of the fifth embodiment of the present invention comprise ligand components, such as the ligand components described with reference to the first, second, third and fourth embodiments of the present invention, complexed with a transition metal and a Lewis acid. Preferred catalyst systems of the fifth embodiment of the present invention include catalyst systems wherein the Lewis acid is bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to the transition metal.

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Examples of catalyst systems comprising a Lewis acid - ligand - transition metal complex of the fifth embodiment of the present invention include **XIX**:



5

wherein

R₃, R₄, L, and T are defined as above.

Complex **XIX** may be produced by synthesizing the transition metal - ligand complex in the manner described above and exemplified in the example herein, and then combining the transition metal - ligand complex with the Lewis acid component.

10

A process of the present invention utilizing the fifth embodiment may be described as follows.

A process for preparing polyolefins comprising contacting one or more olefin monomers with a catalyst system at a temperature and a pressure sufficient to effect polymerization, wherein the catalyst system comprises a transition metal-ligand-Lewis acid complex, e.g. complex **XIX** of the fifth embodiment of the present invention.

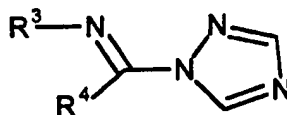
15

Preferred polyolefin products will have a degree of polymerization (DP) of at least 10. A preferred olefin monomer is R'CH=CHR'' wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin. Preferred temperature conditions are -100 to 200 °C. Preferred pressure conditions are from about 1 atmosphere to 100 atmospheres.

20

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A preferred embodiment of the present invention involves a composition comprising (i) a Group 8-10 transition metal M, (ii) one or more Lewis acids, and (iii) a binucleating or multinucleating compound of the formula XVIII:



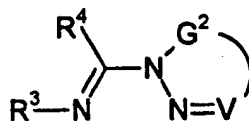
XVIII

wherein the Lewis acid or acids are bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to the transition metal M;

R³ is hydrocarbyl or substituted hydrocarbyl;

R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl.

A preferred embodiment of the present invention involves a composition comprising (i) a Group 8-10 transition metal M, (ii) one or more Lewis acids, and (iii) a binucleating or multinucleating compound of the formula VI:



VI

wherein the Lewis acid or acids are bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to the transition metal M;

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R^3 is hydrocarbyl or substituted hydrocarbyl;

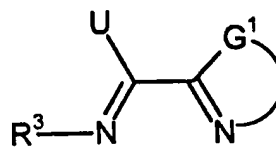
R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

V is CR^6 , N, or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus.

A preferred embodiment of the present invention involves a composition comprising (i) a Group 8-10 transition metal M, (ii) one or more Lewis acids, and (iii) a binucleating or multinucleating compound of the formula IX:



IX

wherein the Lewis acid or acids are bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to a transition metal M;

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

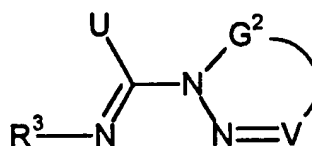
U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

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G¹ is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G¹, C, and N.

A preferred embodiment of the present invention involves a composition comprising (i) a Group 8-10 transition metal M, (ii) one or more Lewis acids, and (iii) a binucleating or multinucleating compound of the formula XII:



XII

wherein the Lewis acid or acids are bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to a transition metal M;

R³ is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR⁴, SR⁴, SeR⁴ or NR⁴R⁸;

R⁴ and R⁸ are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R⁴ and R⁸ may collectively form a ring with nitrogen;

V is CR⁶, N, or PR⁶R⁹;

R⁶ and R⁹ are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R⁶ and R⁹ may collectively form a ring with phosphorus;

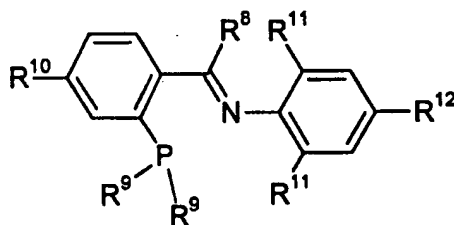
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G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N.

5 The features and advantages of the present invention are further illustrated by the following examples. The procedures described in each example were conducted utilizing conventional laboratory equipment known to those of ordinary skill in the art.

10

Ligand Synthesis



- A1: $R^8 = H$, $R^9 = Ph$, $R^{10} = H$, $R^{11} = tBu$, $R^{12} = tBu$
 15 A2: $R^8 = H$, $R^9 = Ph$, $R^{10} = OMe$, $R^{11} = iPr$, $R^{12} = H$
 A3: $R^8 = H$, $R^9 = Ph$, $R^{10} = H$, $R^{11} = iPr$, $R^{12} = H$
 A4: $R^8 = Me$, $R^9 = Ph$, $R^{10} = H$, $R^{11} = iPr$, $R^{12} = H$
 A5: $R^8 = Ph$, $R^9 = Ph$, $R^{10} = H$, $R^{11} = iPr$, $R^{12} = H$
 A6: $R^8 = H$, $R^9 = Cy$, $R^{10} = H$, $R^{11} = iPr$, $R^{12} = H$
 20 A7: $R^8 = Me$, $R^9 = Cy$, $R^{10} = H$, $R^{11} = iPr$, $R^{12} = H$
 A8: $R^8 = Ph$, $R^9 = Cy$, $R^{10} = H$, $R^{11} = iPr$, $R^{12} = H$

wherein, H = hydrogen; Ph = phenyl; tBu = t-butyl; OMe = methoxy; iPr = isopropyl; Me = methyl; and Cy = cyclohexyl.

25

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Example 1Synthesis of A1.

5 Equimolar amounts of diphenylphosphinobenzaldehyde and 2,4,6-tri-
tert-butylaniline were dissolved in toluene and treated with anhydrous
magnesium sulfate and catalytic *p*-toluenesulfonic acid. The reaction was
refluxed overnight. Water was added, and the organic layer was washed
successively with saturated sodium bicarbonate and brine. After drying
10 over sodium sulfate, the organic extracts were filtered and concentrated to
an oil. Purification by flash chromatography (hexane/EtOAc = 95:5)
provided the desired iminophosphine, which was recrystallized from
ethanol.

15

Example 2Synthesis of A2

 Equimolar amounts of 2,6-diisopropylaniline and 4-
20 methoxybenzaldehyde were refluxed in ethanol for six hours. Upon cooling,
the desired imine precipitated from solution and was recrystallized from
ethanol.

 A solution of the imine (590 mg) in methanol (6 mL) was added to a
suspension of Li_2PdCl_4 (260 mg) in methanol (4 mL). The reaction was
25 stirred at room temperature for 4 hours, at which point the precipitated
cyclopalladate complex was isolated by filtration and used without further
purification.

 A solution of potassium diphenylphosphide (1 mL of 0.5 M solution)
in THF (tetrahydrofuran) was added to a mixture of the cyclopalladate (108
30 mg) and triphenylphosphine (100 mg). After 30 minutes, EtOAc (ethyl
acetate) was added to the reaction flask and the solution was washed

- 49 -

successively with water and brine, then dried over sodium sulfate and concentrated to a syrup. Purification by flash chromatography (hexane/EtOAc = 99:1) provided the desired iminophosphine **A2** (53 mg).

5

Example 3

Synthesis of A3.

A solution of 2,6-diisopropylaniline (640 μ L, 3.39 mmol) and 2-(diphenylphosphino)benzaldehyde (0.98 g, 3.38 mmol) in ethanol (7 mL) was refluxed for six hours. Upon cooling to room temperature, the product crystallized. The yellow crystals were collected by filtration, then recrystallized from ethanol to give the iminophosphine ligand in 69% yield (1.04 g).

15

Example 4

Synthesis of A4.

20

A cooled solution of 2'-fluoroacetophenone (0.77 mL, 6.25 mmol) and 2,6-diisopropylaniline (2.8 mL, 14.8 mmol) in toluene (4 mL) was treated with TiCl_4 (3 mL of 1.0M solution in toluene). The resulting suspension was allowed to warm to room temperature and stirred overnight. The suspension was filtered through alumina, rinsing with ethyl acetate. The filtrate was concentrated to an oil, which was purified by flash chromatography to yield the imine.

25

A solution of the imine (172 mg, 0.58 mmol) in ether was added to a solution of potassium diphenylphosphide in THF (1.2 mL of 0.5M solution). After 3 hours, ethyl acetate and water were added. The layers were

30

- 50 -

separated, and the organic layer was washed with brine, dried over sodium sulfate, filtered, and concentrated to an oil. Purification by flash chromatography (Hexane/EtOAc = 98:2) provided the iminophosphine (200 mg, 0.43 mmol) in 74% yield.

5

Example 5

Synthesis of A5.

10 2-Fluorobenzophenone (0.5 mL) was added to a solution of potassium diphenylphosphide in THF (6 mL of 0.5 M solution). Heat was evolved and the reaction immediately turned green. The reaction went to apparent completion within minutes. After removal of solvent, the residue was dissolved in EtOAc and washed with water and brine, dried over
15 sodium sulfate, filtered, and concentrated. A portion of this material was used directly in the next step to form the imine.

 The crude phosphine (about 2/3 of the total material) was treated with 2,6-diisopropylaniline (1.2 mL), dissolved in toluene (6 mL), and cooled in a dry ice/acetone bath. A solution of TiCl_4 (1.5 mL of a 1.0 M solution) in
20 toluene was added. The reaction was allowed to warm to room temperature and stirred for 24 hours. After addition of EtOAc, the suspension was filtered through silica gel, and the filtrate was concentrated, then purified by flash chromatography (Hexane/EtOAc = 98:2) to provide the iminophosphine A5.

25

Example 6

Synthesis of A6.

30

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Ethanol (10 mL) was added to 2-bromobenzaldehyde (1.17 mL) and 2,6-diisopropylaniline (1.88 mL) and refluxed for 1 hour. The solution was concentrated, and solidified upon introduction of water. The solid was recrystallized from ethanol to yield the imine.

5 A solution of butyl lithium in hexanes (1.75 mL of 1.6 M solution, 2.8 mmol) and ether (5 mL) was treated at -78°C with dicyclohexylphosphine (0.55 mL, 2.75 mmol) and stirred 10 minutes before addition of a solution of the imine (857 mg, 2.49 mmol) in ether (6 mL). The reaction was allowed to warm to room temperature, stirred 18 hours, and worked up using
10 standard extraction techniques. After drying over sodium sulfate, the organic extracts were filtered and concentrated to an oil. Purification by flash chromatography (hexane/EtOAc = 98:2) provided the desired iminophosphine **A6**.

15

Example 7

Synthesis of A7

20 A cooled solution of acetophenone (4 mmol) and 2,6-diisopropylaniline (10 mmol) in toluene (5 mL) was treated with a solution of TiCl_4 (2 mmol) in toluene (2 mL). After stirring 24 hours, the reaction contents were filtered through alumina, and the filtrate was concentrated, then purified by flash chromatography (hexane/EtOAc = 98:2) to provide the imine.

25 A suspension of Li_2PdCl_4 and sodium acetate in warm methanol was treated with an equimolar solution of the imine in methanol. After stirring overnight at room temperature, the precipitated cyclopalladate complex was isolated by filtration.

30 A chilled suspension of the cyclopalladate (174 mg) and triphenylphosphine (200 mg) in ether (2 mL) was treated with a solution of lithium dicyclohexylphosphide in ether/hexanes (0.67 mmol, generated by

- 52 -

addition of dicyclohexylphosphine to a solution of BuLi in ether/hexanes). Tetrahydrofuran was also added as a co-solvent. After 24 hours, the reaction contents were filtered through alumina, then concentrated to an oil. Purification by flash chromatography (hexane/EtOAc = 98:2) provided the
5 desired iminophosphine A7.

Example 8

Synthesis of A8

10

A cooled solution of benzophenone (4 mmol) and 2,6-diisopropylaniline (10 mmol) in toluene (5 mL) was treated with a solution of TiCl₄ (2 mmol) in toluene (2 mL). After stirring 24 hours, the reaction contents were filtered through alumina, eluting with EtOAc. The filtrate was
15 washed successively with saturated sodium bicarbonate solution, 1 M HCl, and brine. After drying over sodium sulfate, filtration, and concentration, the imine was recrystallized from EtOAc.

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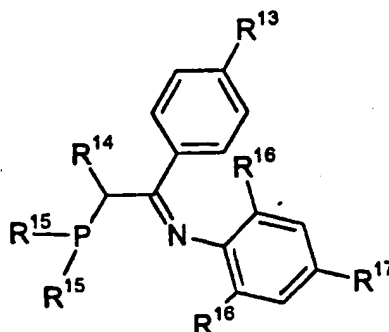
A suspension of Li₂PdCl₄ and sodium acetate in warm methanol was treated with an equimolar solution of the imine in methanol. After stirring overnight at room temperature, the precipitated cyclopalladate complex was isolated by filtration.

25

A chilled suspension of the cyclopalladate (42 mg) and triphenylphosphine (50 mg) in ether (2 mL) was treated with a solution of lithium dicyclohexyl phosphide in ether/hexanes (0.17 mmol, generated by
addition of dicyclohexylphosphine to a solution of BuLi in ether/hexanes). Tetrahydrofuran was also added as a co-solvent. After 24 hours, the reaction contents were filtered through alumina, then concentrated to an oil. Purification by flash chromatography (hexane/EtOAc = 98:2) provided the
desired iminophosphine A8.

30

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A9: $R^{13} = H$, $R^{14} = H$, $R^{15} = Ph$, $R^{16} = iPr$, $R^{17} = H$

5 A10: $R^{13} = CF_3$, $R^{14} = H$, $R^{15} = Ph$, $R^{16} = iPr$, $R^{17} = H$

A11: $R^{13} = H$, $R^{14} = CH_3$, $R^{15} = Ph$, $R^{16} = iPr$, $R^{17} = H$

wherein CH_3 = methyl; CF_3 = trifluoromethyl; and the other terms are as described above with reference to A1 – A8.

10

Example 9

Synthesis of A9

15 A cooled solution of acetophenone (4 mmol) and 2,6-diisopropylaniline (12 mmol) in toluene (5 mL) was treated with a solution of $TiCl_4$ (2 mmol) in toluene (2 mL). After stirring 24 hours, the reaction contents were filtered through alumina, and the filtrate was concentrated, then purified by flash chromatography (hexane/EtOAc = 98:2) to provide the

20 imine.

A solution of the imine in ether was treated with a slight excess of LDA (generated by the addition of BuLi to diisopropylamine) at $-78^\circ C$ and allowed to gradually warm to room temperature over the course of an hour. After cooling the reaction flask in a dry ice/acetone bath,

- 54 -

chlorodiphenylphosphine (0.95 eq) was added. After four hours, the reaction contents were filtered through silica gel and concentrated to an oil. The desired β -iminophosphine **A9** is unstable, and was used directly to form the bidentate metal complex with Ni(II).

5

Example 10

Synthesis of A10

10 A cooled solution of 4'-trifluoromethylacetophenone (5 mmol) and 2,6-diisopropylaniline (15 mmol) in toluene (5 mL) was treated with a solution of TiCl_4 (2.5 mmol) in toluene (2.5 mL). After stirring 24 hours, the reaction contents were filtered through alumina, and the filtrate was concentrated to a solid, which was recrystallized from EtOAc to provide the
15 imine.

A solution of the imine (149 mg, 0.43 mmol) in ether was treated with a slight excess of LDA (0.5 mmol, generated by the addition of BuLi to diisopropylamine) at -78°C and allowed to gradually warm to room temperature over the course of an hour. After cooling the reaction flask in a
20 dry ice/acetone bath, chlorodiphenylphosphine (0.4 mmol) was added. After four hours, the reaction contents were filtered through silica gel and concentrated to an oil. Purification by flash chromatography (hexane/EtOAc = 98:2) provided the desired β -iminophosphine **A10** with trace impurities.

25

Example 11

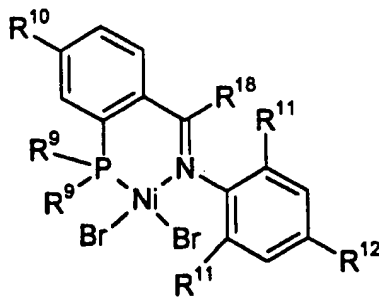
Synthesis of A11.

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A cooled solution of propiophenone (4 mmol) and 2,6-diisopropylaniline (12 mmol) in toluene (5 mL) was treated with a solution of TiCl_4 (2 mmol) in toluene (2 mL). After stirring 24 hours, the reaction contents were filtered through alumina, and the filtrate was concentrated to a syrup, which was purified by flash chromatography (hexane/EtOAc = 98:2) to give the desired imine.

A solution of the imine (195 mg, 0.67 mmol) in ether was treated with a slight excess of LDA (0.75 mmol, generated by the addition of BuLi to diisopropylamine) at -78°C and allowed to gradually warm to room temperature over the course of an hour. After cooling the reaction flask in a dry ice/acetone bath, chlorodiphenylphosphine (0.6 mmol) was added. After four hours, the reaction contents were filtered through silica gel and concentrated to an oil. The desired product **A11** was not stable to conventional flash chromatography, and thus the residue was used directly to form a catalyst precursor metal complex.

Synthesis of the Metal Complex



20

B1: $\text{R}^8 = \text{H}$, $\text{R}^9 = \text{Ph}$, $\text{R}^{10} = \text{H}$, $\text{R}^{11} = \text{tBu}$, $\text{R}^{12} = \text{tBu}$

B2: $\text{R}^8 = \text{H}$, $\text{R}^9 = \text{Ph}$, $\text{R}^{10} = \text{OMe}$, $\text{R}^{11} = \text{iPr}$, $\text{R}^{12} = \text{H}$

B3: $\text{R}^8 = \text{H}$, $\text{R}^9 = \text{Ph}$, $\text{R}^{10} = \text{H}$, $\text{R}^{11} = \text{iPr}$, $\text{R}^{12} = \text{H}$

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B4: $R^8 = \text{Me}$, $R^9 = \text{Ph}$, $R^{10} = \text{H}$, $R^{11} = \text{iPr}$, $R^{12} = \text{H}$

B5: $R^8 = \text{Ph}$, $R^9 = \text{Ph}$, $R^{10} = \text{H}$, $R^{11} = \text{iPr}$, $R^{12} = \text{H}$

B6: $R^8 = \text{H}$, $R^9 = \text{Cy}$, $R^{10} = \text{H}$, $R^{11} = \text{iPr}$, $R^{12} = \text{H}$

B7: $R^8 = \text{Me}$, $R^9 = \text{Cy}$, $R^{10} = \text{H}$, $R^{11} = \text{iPr}$, $R^{12} = \text{H}$

5 **B8:** $R^8 = \text{Ph}$, $R^9 = \text{Cy}$, $R^{10} = \text{H}$, $R^{11} = \text{iPr}$, $R^{12} = \text{H}$

wherein the terms are as described above with reference to examples 1-11.

Example 12

10

Synthesis of B3

The iminophosphine **A3** (88 mg, 1.96×10^{-4} mol) and (DME)NiBr₂ (53mg, 1.8×10^{-4} mol) were combined as solids in an inert atmospheres glove box. The Schlenk flask was removed from the glove box and to the flask was added 10 mL of dry CH₂Cl₂. The deep orange/brown solution was left to stir at 23° C for 6 hours. The solvent was evaporated under reduced pressure resulting in a red/brown powder. The solid was washed with 3 x 15 mL of hexane and then placed under high vacuum to remove all solvent. 64 mg of pre-catalyst **B3** was isolated (70 % yield).

20

Example 13

Synthesis of B4

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The iminophosphine **A4** (122 mg, 0.26 mmol) and (DME)NiBr₂ (77mg 0.25mmol) were combined in a Schlenk flask with 20 mL of CH₂Cl₂. The deep brown solution was left to stir at 23° C for 2 days. The solvent was evaporated under reduced pressure resulting in a brown powder. The solid was washed with 3 x 10 mL of diethyl ether and then placed under

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high vacuum to remove all solvent. 90 mg of pre-catalyst **B4** was isolated (53 % yield).

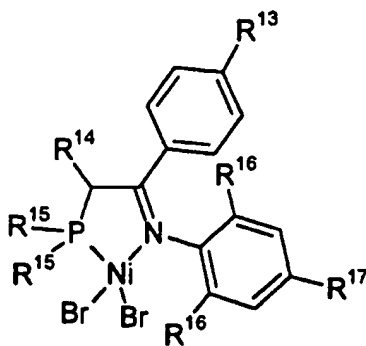
Example 14

5

Synthesis of B5

The iminophosphine **A5** (60 mg, 0.114 mmol) and (DME)NiBr₂ (35mg 0.113mmol) were combined in a Schlenk flask with 15 mL of CH₂Cl₂.
 10 The deep brown solution was left to stir at 23° C overnight. The solvent was evaporated under reduced pressure resulting in a brown powder. The solid was washed with 2 x 10 mL of hexane and then placed under high vacuum to remove all solvent. 49 mg of pre-catalyst **B5** was isolated (60 % yield).

15



B9: R¹³ = H, R¹⁴ = H, R¹⁵ = Ph (phenyl), R¹⁶ = iPr (isopropyl), R¹⁷ = H

B10: R¹³ = CF₃, R¹⁴ = H, R¹⁵ = Ph, R¹⁶ = iPr, R¹⁷ = H

20 **B11:** R¹³ = H, R¹⁴ = CH₃, R¹⁵ = Ph, R¹⁶ = iPr, R¹⁷ = H

wherein all terms are as described with reference to examples 1-11 above.

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Example 15Synthesis of B9

5 A CH₂Cl₂ solution of the iminophosphine **A9** (50 mg, 0.11 mmol) was transferred via cannula onto a suspension of (DME)NiBr₂ (34 mg 0.11 mmol) in 10 mL of CH₂Cl₂. The resulting deep brown solution was left to stir at 23° C for 3 hours. The solvent was evaporated under reduced pressure resulting in a brown powder. The solid was washed with 3 x 10 mL of
10 hexane and then placed under high vacuum to remove all solvent affording **B9**.

Olefin Polymerization

15

Example 16

The iminophosphine complex **B3** (10 mg, 1.5×10^{-5} mol) was dissolved in 50 mL of dry toluene. The reaction mixture was cooled to 0° C
20 and placed under an ethylene atmosphere. 3.0 mL of (~ 350 eq) of MAO (10 % by weight in toluene) was added to the polymerization flask. The mixture was left to stir for one hour at room temperature. Acetone, 6M HCl, and H₂O were added to quench the polymerization and precipitate the polyethylene. The polymer was isolated and dried *in vacuo*. ¹H NMR
25 analysis is consistent with branched polyethylene having 57 branches/1000 carbon atoms.

Example 17

30 The iminophosphine complex **B4** (15 mg, 2.2×10^{-5} mol) was dissolved in 50 mL of dry toluene. The reaction mixture was cooled to 0° C

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and placed under an ethylene atmosphere. 3.0 mL of (~ 350 eq) of MAO (10 % by weight in toluene) was added to the polymerization flask. The mixture was left to stir for one hour at room temperature. Acetone, 6M HCl, and H₂O were added to quench the polymerization and precipitate the polyethylene. ~ 50 mg of polymer was isolated and dried *in vacuo*. ¹H NMR analysis is consistent with branched polyethylene and DSC indicates T_m = 118° C. GPC: M_w = 15,000

Example 18

The iminophosphine complex B5 (9 mg, 1.2 x 10⁻⁵ mol) was dissolved in 50 mL of dry toluene. The reaction mixture was cooled to 0° C and placed under an ethylene atmosphere. Approximately 100 eq of MAO (10 % by weight in toluene) was added to the polymerization flask. The mixture was left to stir for one hour at 0° C. Acetone, 6M HCl, and H₂O were added to quench the polymerization and precipitate the polyethylene. The polymer was dried *in vacuo* resulting in 125 mg of polymer. ¹H NMR analysis is consistent with branched polyethylene (35 branches/1000 carbon atoms). DSC: T_m = 109° C. GPC: M_w = 15,000

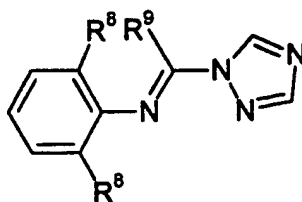
Example 19

The iminophosphine complex B9 (~20 mg) was dissolved in 50 mL of dry toluene. The reaction mixture was cooled to 0° C and placed under an ethylene atmosphere. Approximately 200 eq of MAO (10 % by weight in toluene) was added to the polymerization flask. The mixture was left to stir for 20 minutes at 0° C. The mixture was left to stir for an additional 25 minutes at 23° C. Acetone, 6M HCl, and H₂O were added to quench the polymerization and precipitate the polyethylene. The polymer was dried *in vacuo* resulting in 30 mg of polymer. ¹H NMR analysis is consistent with

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branched polyethylene (40 branches/1000 carbon atoms) and DSC indicates $T_m = 114^\circ \text{C}$. GPC: $M_w = 400,000$.

5 Ligand Synthesis



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C1: $R^8 = \text{Me}$, $R^9 = 1\text{-naphthyl}$

C2: $R^8 = i\text{Pr}$, $R^9 = 1\text{-naphthyl}$

C3: $R^8 = \text{Me}$, $R^9 = \text{phenyl}$

C4: $R^8 = i\text{Pr}$, $R^9 = \text{phenyl}$

C5: $R^8 = i\text{Pr}$, $R^9 = 2,6\text{-dimethoxyphenyl}$

15

Example 20

Synthesis of C1. Equimolar amounts of 1,2,4-triazole and *N*-(2,6-dimethylphenyl)-1-naphthimidoyl chloride (derived in the conventional fashion [H. Ulrich, *The Chemistry of Imidoyl Halides*, Plenum, New York, 1968] from the corresponding amide and phosphorus pentachloride) were treated with an excess of triethylamine in methylene chloride at room temperature. After 1 hour, the solution was concentrated, taken up in ethyl acetate, filtered, and washed sequentially with saturated sodium bicarbonate solution, 0.5M HCl solution, and brine, then dried over

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- 61 -

magnesium sulfate, filtered, and concentrated to a syrup. Purification by flash chromatography (hexane/EtOAc = 4:1) afforded the triazole/imine ligand **C1** as a pale yellow solid.

5

Example 21

Synthesis of C2. A mixture of 1,2,4-triazole (1.2 mmol) and N-(2,6-diisopropylphenyl)-1-naphthimidoyl chloride (0.5 mmol) was treated with triethylamine (1 mmol) and methylene chloride (5 mL) and stirred four hours at room temperature. The reaction was worked up as described in example 20 to afford **C2** as a pale yellow solid.

10

Example 22

Synthesis of C3. A mixture of 1,2,4-triazole (2.9 mmol) and N-(2,6-dimethylphenyl)-1-benzimidoyl chloride (1.5 mmol) was treated with triethylamine (1.5 mmol) and methylene chloride (7 mL) and stirred 14 hours at room temperature. The reaction was worked up as described in example 20 to afford **C3** as a pale yellow solid (242 mg).

15

Example 23

Synthesis of C4. A mixture of 1,2,4-triazole (1.5 mmol) and N-(2,6-diisopropylphenyl)-1-benzimidoyl chloride (0.7 mmol) was treated with triethylamine (1 mmol) and methylene chloride (6 mL) and stirred overnight at room temperature. The reaction was worked up as described in example 20 to afford **C4** as a pale yellow solid (85 mg) after purification by flash chromatography (hexane/EtOAc = 3:1).

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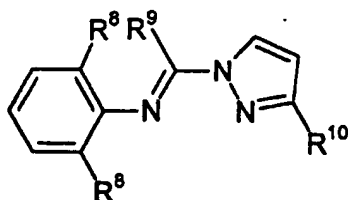
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Example 24

Synthesis of C5. 2,6-Diisopropylaniline (25 mmol) was added to a chilled suspension of 2,6-dimethoxybenzoyl chloride (25 mmol) in pyridine (20 mL).

5 After stirring three hours, water (50 mL) was added, preparing a purple precipitate that was isolated by filtration and subsequently recrystallized from ethanol to provide the amide as a purple solid.

A solution of the amide (690 mg, 2 mmol) in acetonitrile (8 mL) was added to a mixture formed by the addition of triethylamine (580 μ L) to a
10 cooled suspension of 1,2,4-triazole (420 mg, 6 mmol) and POCl_3 in acetonitrile (8 mL). After stirring 24 hours at room temperature, the reaction contents were filtered, and the filtrate was evaporated to an oil. The oil was dissolved in EtOAc, and washed successively with aqueous solutions of sodium bicarbonate, HCl, and NaCl. The organic layer was dried over
15 magnesium sulfate, filtered, and concentrated to an oil. Purification by flash chromatography (hexane/EtOAc = 3:1) afforded the desired imino-substituted heterocyclic C5.



20

C6: $\text{R}^8 = \text{Me}$, $\text{R}^9 = 1\text{-naphthyl}$, $\text{R}^{10} = \text{CH}_3$

C7: $\text{R}^8 = \text{iPr}$, $\text{R}^9 = 1\text{-naphthyl}$, $\text{R}^{10} = \text{CH}_3$

C8: $\text{R}^8 = \text{Me}$, $\text{R}^9 = 1\text{-naphthyl}$, $\text{R}^{10} = \text{H}$

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Example 25

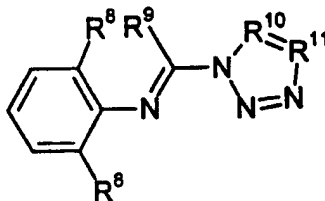
Synthesis of C6. A mixture of 3-methylpyrazole (0.8 mmol) and *N*-(2,6-dimethylphenyl)-1-naphthimidoyl chloride (0.8 mmol) was treated with triethylamine (1.5 mmol) and methylene chloride (5 mL) and stirred 4 hours at room temperature. The reaction was worked up as described in example 20 to afford the desired pyrazole/imine C6.

Example 26

Synthesis of C7. A mixture of 3-methylpyrazole (1.0 mmol) and *N*-(2,6-diisopropylphenyl)-1-naphthimidoyl chloride (0.7 mmol) was treated with triethylamine (1.0 mmol) and methylene chloride (5 mL) and stirred 1 hour at room temperature. The reaction was worked up as described in example 20 to afford the desired pyrazole/imine C7.

Example 27

Synthesis of C8. A mixture of pyrazole (4.0 mmol) and *N*-(2,6-dimethylphenyl)-1-naphthimidoyl chloride (1.5 mmol) was treated with triethylamine (2.0 mmol) and methylene chloride (8 mL) and stirred 16 hours at room temperature. The reaction was worked up as described in example 20 to afford the desired pyrazole/imine C8 as pale yellow crystals.



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C9: R⁸ = iPr; R⁹ = 1-naphthyl; R¹⁰, R¹¹ = C

C10: R⁸ = iPr; R⁹ = phenyl; R¹⁰, R¹¹ = C-Ph and N (one C, one N)

5

Example 28

Synthesis of C9. A mixture of 1*H*-1,2,3-triazole (100 µL) and *N*-(2,6-diisopropylphenyl)-1-naphthimidoyl chloride (200 mg) was treated with triethylamine (150 µl) and methylene chloride (6 mL) and stirred 1 hour at room temperature. The reaction was worked up as described in example 20 to afford the desired triazole/imine **C9**.

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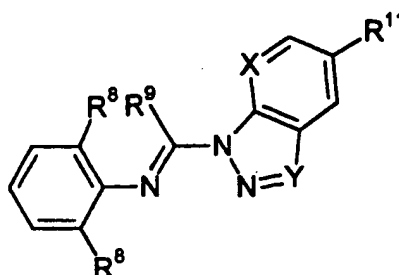
Example 29

Synthesis of C10. A mixture of 5-phenyl-1*H*-tetrazole (160 mg, 1.1 mmol) and *N*-(2,6-diisopropylphenyl)-1-benzimidoyl chloride (0.7 mmol) was treated with triethylamine (250 µl) and methylene chloride (6 mL) and stirred 16 hours at room temperature. The reaction was worked up as described in example 20. Attempts to further purify the desired product using silica gel chromatography led to ligand decomposition, and thus the crude product of the workup was used directly in the next step to form the nickel complex **D10**.

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C11: $R^8 = iPr$; $R^9 = \text{phenyl}$; $R^{11} = \text{COOH}$; $X = \text{CH}$; $Y = \text{N}$

C12: $R^8 = iPr$; $R^9 = \text{phenyl}$; $R^{11} = \text{H}$; $X = \text{N}$; $Y = \text{N}$

C13: $R^8 = iPr$; $R^9 = \text{CF}_3$; $R^{11} = \text{H}$; $X = \text{CH}$; $Y = \text{CH}$

C14: $R^8 = iPr$; $R^9 = \text{CF}_3$; $R^{11} = \text{NO}_2$; $X = \text{CH}$; $Y = \text{CH}$

5

Example 30

Synthesis of C11. A mixture of benzotriazole-5-carboxylic acid (163 mg, 1.0 mmol) and *N*-(2,6-diisopropylphenyl)-1-benzimidoyl chloride (0.7 mmol) was treated with triethylamine (260 μl) and methylene chloride (6 mL) and stirred overnight at room temperature. The reaction was worked up as described in example 20 and purified by flash chromatography (hexane/ethyl acetate = 3:1) to afford the desired benzotriazole/imine **C11**, as well as a contaminant byproduct (MS = 689) which may be the diacylated product resulting from acylation of both the desired ring nitrogen and the carboxylic acid.

10

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Example 31

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Synthesis of C12 A mixture of 1*H*-1,2,3-triazolo(4,5- β)pyridine (1.0 mmol) and *N*-(2,6-diisopropylphenyl)-1-benzimidoyl chloride (0.5 mmol) was treated with triethylamine (1.0 mmol) and methylene chloride (7 mL) and

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stirred 16 hours at room temperature. The reaction was worked up as described in example 20 and used directly without further purification.

Example 32

5

Synthesis of C13 A solution of indazole (202 mg, 1.71 mmol) in THF (5.0 mL) was cooled to 0 °C in an ice bath and treated with NaH (60% dispersion in mineral oil, 106 mg, 2.66 mmol). The resulting suspension was stirred at 0 °C for 25 min, then treated with N-(2,6-diisopropylphenyl)-trifluoroacetimidoyl chloride (497 mg, 1.70 mmol) [which had been prepared according to the procedure of K. Tamura, *et al.*, *J. Org. Chem.* **1993**, *58*, 32-35, from trifluoroacetic acid, 2,6-diisopropyl aniline, carbon tetrachloride, triphenylphosphine and triethylamine] via syringe, rinsing the syringe with THF (0.5 mL). The ice bath was removed, and the suspension allowed to stir at rt for 1.5h. The solvent was removed *in vacuo*, and the residue was partitioned between saturated NaHCO₃ (5 mL) and CH₂Cl₂ (5 mL). The aqueous layer was further extracted with CH₂Cl₂ (2 X 5 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated in vacuo. The resulting residue was flash chromatographed (SiO₂, 4% EtOAc : Hex) to afford **C13** (548 mg, 86%): R_f 0.27 (4% EtOAc : Hex); ¹H-NMR (300 MHz, CDCl₃) δ 8.45 (d, 1 H, J = 8.2 Hz), 8.29 (d, 1 H, J = 0.6 Hz), 7.84 (dt, 1 H, J = 8.0 Hz, J = 1.1 Hz), 7.54 (ddd, 1H, J = 8.4 Hz, J = 7.1 Hz, J 1.1 Hz), 7.40 (ddd, 1 H, J = 8.0 Hz, J = 7.1 Hz, J = 0.8 Hz), 7.06-7.20 (m, 3H), 2.85 (p, 2H, J = 6.9 Hz), 1.20 (d, 6H, J = 6.9 Hz), 1.15 (d, 6 H, J = 6.6 Hz); IR (film) 2965, 1684, 1431, 1171, 1154, 926 cm⁻¹; FDMS *m/z* 373 (M⁺, 100%).

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C13 was contaminated with a small amount of unidentified impurities: ¹H NMR (300 MHz, CDCl₃) δ 7.72 (d, J = 9.1 Hz), 2.72 (d, J = 6.9 Hz).

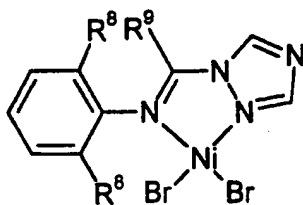
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Example 33

Synthesis of C14 A solution of 5-nitroindazole (286 mg, 1.75 mmol) in THF (5 mL) was cooled to 0 °C in an ice bath and treated with NaH (60% dispersion in mineral oil, 110 mg, 2.74 mmol). The resulting suspension was stirred at 0 °C for 20 min, then treated with N-(2,6-diisopropylphenyl)-trifluoroacetimidoyl chloride (509 mg, 1.74 mmol) via syringe, rinsing the syringe with THF (0.5 mL). The ice bath was removed, and the suspension stirred at rt for 2 h. The solvent was removed *in vacuo*, and the residue partitioned between saturated NaHCO₃ (5 mL) and CH₂Cl₂ (5 mL). The aqueous layer was further extracted with CH₂Cl₂ (2 X 5 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was flash chromatographed (3% EtOAc : Hex) to afford **C14** (573 mg, 78%): R_f 0.16 (3% EtOAc : Hex); ¹H NMR (300 MHz, CDCl₃) δ 8.80 (dd, 1 H, J = 2.2 Hz, J = 0.5 Hz), 8.47 (s, 1H), 8.42 (dd, 1H, J = 9.2 Hz, J = 1.9 Hz), 8.12 (dd, 0.5 H, J = 9.8 Hz, J = 1.9 Hz), 7.85 (d, 0.5 H, J = 9.6 Hz), 7.18-7.22 (m, 3 H), 2.79 (p, 2 H, J = 6.9 Hz), 1.20 (br d, 6 H, J = 5.8 Hz), 1.16 (br d, 6 H, J = 6.0 Hz); IR (Film) 2965, 1686, 1528, 1431, 1345, 1172, 1150, 922; FDMS *m/z* 418 (M⁺, 100%).

C14 was contaminated with a small amount of unidentified impurities: ¹H NMR (300 MHz, CDCl₃) δ 8.52-8.64 (br m), 2.69 (p, J = 6.9 Hz), 0.85-1.10 (br s).



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D1: R⁸ = Me, R⁹ = 1-naphthyl

- 68 -

D2: R⁸ = iPr, R⁹ = 1-naphthylD3: R⁸ = Me, R⁹ = phenylD4: R⁸ = iPr, R⁹ = phenylD5: R⁸ = iPr, R⁹ = 2,6-dimethoxyphenyl

5

Example 34

Synthesis of D1. A methylene chloride solution of the triazole/imine **C1** (46 mg, 0.14 mmol) and (DME)NiBr₂ (37 mg, 0.12 mmol) were combined via stainless steel cannula. The mixture was left to stir at 23 °C for 16 hours. The solvent was partially evaporated under reduced pressure and 10 mL of hexane was added to fully precipitate the complex. The resulting yellow solid was washed with hexane and then placed under high vacuum to remove all solvent. 37 mg of pre-catalyst **D1** isolated (60 % yield).

15

Example 35

Synthesis of D2. A flame dried Schlenk flask equipped with a magnetic stir bar and capped with a rubber septum. To the flask was added DMENiBr₂ (59 mg, 0.191 mmol) and 10 mL of methylene chloride. In a separate flask the imine/triazole **C2** (78 mg, 0.204mmol) was dissolved in 5 mL of methylene chloride and transferred via stainless steel canula onto the DMENiBr₂ suspension. The mixture was stirred at room temperature for 16 hours. After 16 hours, the methylene chloride was removed *in vacuo* resulting in a yellow/green solid. The solid was washed with 2 X 10 mL of hexane. The solid was left to dry under reduced pressure for several hours resulting in 42 mg of the imine/triazole complex **D2**.

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Example 36

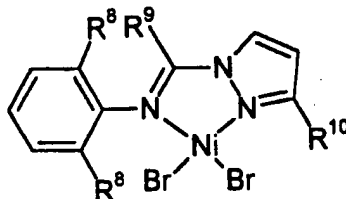
5 Synthesis of D3. Methylene chloride (8 mL) was added to a mixture of triazole/imine **C3** (54 mg) and (DME)NiBr₂ (57 mg). The reaction was stirred at room temperature overnight. Solvent was removed via filter cannula, and the pale yellow powder was washed with hexane, then dried *in vacuo*.

Example 37

10 Synthesis of D4. Methylene chloride (6 mL) was added to a mixture of triazole/imine **C4** (60 mg) and (DME)NiBr₂ (45 mg). The reaction was stirred at room temperature overnight. The solvent was partially evaporated under a stream of argon, and hexane was added. The precipitated pale
15 green complex was washed several times with hexane, then dried *in vacuo*.

Example 38

20 Synthesis of D5. Methylene chloride (9 mL) was added to a mixture of ligand **C5** (125 mg) and (DME)NiBr₂ (83 mg). The reaction was stirred at room temperature overnight. The solvent was partially evaporated under a stream of argon, and hexane was added. The precipitated pale green complex was washed several times with hexane, then dried *in vacuo*.



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D6: $R^8 = \text{Me}$, $R^9 = 1\text{-naphthyl}$, $R^{10} = \text{CH}_3$ D7: $R^8 = \text{iPr}$, $R^9 = 1\text{-naphthyl}$, $R^{10} = \text{CH}_3$

5

Example 39

Synthesis of D6. Methylene chloride (10 mL) was added to a mixture of the pyrazole/imine ligand D6 (81 mg, 0.24 mmol) and (DME)NiBr₂ (60 mg, 0.19 mmol). The suspension immediately turned a deep orange/brown color, and was allowed to stir 18 hours. The solvent was evaporated under a stream of argon, and the precipitated orange solid was washed several times with hexane and hexane/methylene chloride before drying *in vacuo*. The pre-catalyst F3 was isolated as an orange/brown powder.

15

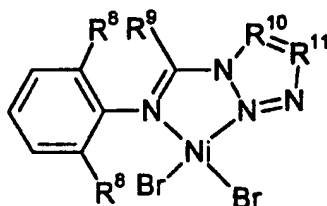
Example 40

Synthesis of D7. A flame dried Schlenk flask equipped with a magnetic stir bar and capped with a rubber septum. To the flask was added DMENiBr₂ (71 mg, 0.23 mmol) and 10 mL of methylene chloride. In a separate flask the imine/heterocyclic C7 (98 mg, 0.25mmol) was dissolved in 5 mL of methylene chloride and transferred via stainless steel canula onto the DMENiBr₂ suspension. The mixture was stirred at room temperature for 16 hours. After 16 hours, the methylene chloride was removed *in vacuo* resulting in a red/brown solid. The solid was washed with 2 X 5 mL of hexane. The solid was left to dry under reduced pressure for several hours resulting in 97 mg of the imine/heterocycle complex D7.

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Synthesis of

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D9: $R^8 = iPr$; $R^9 = 1\text{-naphthyl}$; $R^{10}, R^{11} = C$

D10: $R^8 = iPr$; $R^9 = \text{phenyl}$; $R^{10}, R^{11} = C\text{-Ph and N (one C, one N)}$

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Example 42

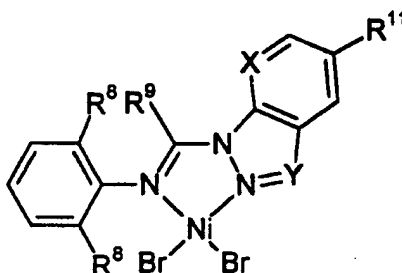
10 Synthesis of D9. Methylene chloride (5 mL) was added to a mixture of the triazole/imine ligand **C9** (42 mg) and (DME)NiBr₂ (200 mg). The suspension was allowed to stir 18 hours, at which time the solvent was evaporated under a stream of argon, and the precipitated yellow-orange solid was washed several times with hexane and hexane/methylene chloride before drying *in vacuo*.
15

Example 43

Synthesis of D10. Methylene chloride (7 mL) was added to a mixture of the tetrazole/imine ligand **C10** (82 mg) and (DME)NiBr₂ (40 mg). The suspension was allowed to stir 18 hours, at which time the solvent was evaporated under a stream of argon, and the precipitate pale green solid was washed several times with hexane and hexane/methylene chloride before drying *in vacuo*.
20

25

- 72 -



D11: $R^8 = iPr$; $R^9 = \text{phenyl}$; $R^{11} = \text{COOH}$, $X = \text{CH}$; $Y = \text{N}$

D12: $R^8 = iPr$; $R^9 = \text{phenyl}$; $R^{11} = \text{H}$; $X = \text{N}$; $Y = \text{N}$

D13: $R^8 = iPr$; $R^9 = \text{CF}_3$; $R^{11} = \text{H}$; $X = \text{CH}$; $Y = \text{CH}$

D14: $R^8 = iPr$; $R^9 = \text{CF}_3$; $R^{11} = \text{NO}_2$; $X = \text{CH}$; $Y = \text{CH}$

Example 44

Synthesis of D11. Methylene chloride (5 mL) was added to a mixture of excess benzotriazole/imine ligand **C11** and $(\text{DME})\text{NiBr}_2$. The reaction was allowed to stir 18 hours, at which time the solvent was evaporated under a stream of argon, and the precipitated beige solid was washed several times with hexane and hexane/methylene chloride before drying *in vacuo*.

Example 45

Synthesis of D12. Methylene chloride was added to a mixture of the benzotriazole/imine ligand **C12** (82 mg) and a deficiency of $(\text{DME})\text{NiBr}_2$. A green precipitate appeared almost immediately. The solvent was evaporated under a stream of argon, and the precipitated pale green solid was washed several times with hexane and hexane/methylene chloride before drying *in vacuo*.

Example 46

- 73 -

Synthesis of D13 A mixture of imine/indazole adduct **C13** (112 mg, 0.299 mmol) and (DME)NiBr₂ (73 mg, 0.238 mmol) was dissolved in CH₂Cl₂ (10 mL). The resulting solution was stirred at rt overnight. The suspension was concentrated under a stream of Ar, and the resulting precipitate was washed several times with hexanes. The precipitate was dried *in vacuo* to afford dibromo complex **D13**.

Example 47

Synthesis of D14 A mixture of imine/indazole adduct **C14** (100 mg, 0.238 mmol) and (DME)NiBr₂ (63 mg, 0.206 mmol) was dissolved in CH₂Cl₂ (10 mL), and stirred at rt overnight. The orange/yellow suspension was concentrated under a stream of Ar, and washed with hexanes (10 mL). The residue was dried *in vacuo* to afford **D14** as an orange solid.

POLYMERIZATIONS

Example 48

The triazole/imine complex **D1** (2.0 mg) was suspended in 50 mL of dry toluene. The reaction mixture was equilibrated at room temperature under an ethylene atmosphere, then treated with MAO (2.0 mL of a 10 % by weight solution in toluene) and stirred under 1 atm ethylene. A white polyethylene precipitate was observed within minutes. After five minutes, the reaction was quenched by the sequential addition of acetone, methanol, and 6M HCl. The precipitate was isolated by filtration, washed, and dried *in vacuo* to yield 700 mg of polyethylene (85,000 To/h). DSC: T_m = 123. GPC: M_w = 23,000.

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Example 49

The triazole/imine complex D3 (2.7 mg) was suspended in 20 mL of dry toluene. The reaction mixture was equilibrated at 0°C under an ethylene atmosphere, then treated with MAO (2.0 mL of a 10 % by weight solution in toluene) and stirred under 1 atm ethylene. After 15 minutes, the reaction was quenched by the sequential addition of acetone, methanol, and 6M HCl. The precipitate was isolated by filtration, washed, and dried *in vacuo* to yield 747 mg of polyethylene. (19,600 To/h, Mn = 6900, Mw = 52,200 (GPC); 2 branches/1000 carbons by NMR)

Example 50

The pyrazole/imine complex D6 (14.6 mg) was suspended in 18 mL of dry toluene. The reaction mixture was cooled to 0°C and placed under an ethylene atmosphere. A 10% by weight solution of MAO in toluene (1.8 mL) was added to the polymerization flask. The ice bath was removed and the mixture was left to stir for thirty minutes with substantial evolution of heat. Acetone, 6M HCl, and H₂O were added to quench the polymerization and precipitate the polyethylene. The polymer was isolated by filtration, washed, and dried *in vacuo*. The procedure was repeated without removing the ice bath, with similar polymer characteristics. In both cases, ¹H NMR analysis was consistent with branched polyethylene of relatively low molecular weight (<5,000).

Example 51

The triazole/imine complex D9 (4.0 mg) was suspended in 18 mL of dry toluene. The reaction mixture was cooled to 0°C and placed under an ethylene atmosphere. A 10% by weight solution of MAO in toluene (1.8

- 75 -

mL) was added to the polymerization flask. The mixture was left to stir for 45 minutes at 0°C. Acetone, 6M HCl, and H₂O were added to quench the polymerization. No precipitated polyethylene was observed. Separation and subsequent evaporation of the aqueous layer yielded a small amount of solid. The reaction was repeated at room temperature, and a small amount of amorphous material was recovered.

Example 52

10 A 250 mL flame dried Schlenk flask was charged with bis(1,5-cyclooctadiene)nickel(0) (14.0 mg, 0.051 mmol), HBAr₄ (Ar = 3,5-bis(trifluoromethyl)phenyl) (39.4 mg, 0.046 mmol) and imine/indazole adduct **C13** (13.7 mg, 0.037 mmol). The flask was evacuated and backfilled with ethylene, then charged with toluene (30 mL) resulting in the formation of a dark green/blue solution. The reaction exothermed to ~ 45 °C, and was allowed to stir under ethylene (1 atm) with no temperature control for 1.5 h, after which it was quenched by the addition of acetone and MeOH. The solvent was removed *in vacuo* to afford an oily waxy solid (2.83g): GPC: M_n = 327; M_w/M_n = 9; ¹H NMR: 92 branches/1000 carbon atoms.

Example 53

25 A 250 mL flame dried Schlenk flask was charged with bis(1,5-cyclooctadiene)nickel(0) (8.5 mg, 0.031 mmol), HBAr₄ (Ar = 3,5-bis(trifluoromethyl)phenyl) (24.3 mg, 0.028 mmol) and imine/indazole adduct **C14** (11.0 mg, 0.026 mmol). The flask was evacuated and backfilled with ethylene, then charged with toluene (30 mL) resulting in the formation of an orange/brown solution. The reaction was allowed to stir under ethylene (1 atm) at rt for ~ 1.33 h, after which it was quenched by the

- 76 -

addition of acetone and MeOH. The resulting polyethylene was collected by vacuum filtration, and dried *in vacuo* to afford a white polyethylene (117.2 mg): GPC: $M_n = 5710$; $M_w/M_n = 4.7$; $^1\text{H NMR}$: 42 branches/1000 carbon atoms.

5

Example 54

A flame dried Schlenk flask was charged with complex **D7** (6 mg, 0.0098 mmol) and 50 mL of toluene. The flask was then cooled to 0 C in an ice bath. MAO (1.5 mL of a 10 wt.% solution in toluene) was then added to the suspension and the reaction left to stir for 30 minutes. Acetone, methanol and 6M HCl were added to quench the reaction and precipitate the resulting branched polyethylene ($^1\text{H NMR } M_n = 2500$).

10

Example 55

A flame dried Schlenk flask was charged with complex **D1** (5 mg, 0.0092 mmol), norbornene (2g) and 50 mL of toluene. The flask was then placed in a water bath (23 C) to control reaction temperature. MAO (2 mL of a 10 wt.% solution in toluene) was then added to the suspension and the reaction left to stir for 16 hours. Acetone and methanol were added to quench the reaction and precipitate the resulting polynorbornene. The polymer was collected by filtration and washed with 6M HCl, water, and acetone. The polymer was dried in a vacuum oven resulting in 700 mg of polynorbornene. GPC: $M_n = 14,500$; $M_w = 44,000$.

20

Example 56

A flame dried Schlenk flask was charged with complex **D4** (6 mg, 0.0091 mmol), 1 atmosphere ethylene and 50 mL of toluene. The flask was then placed in a water bath (23 C) to control reaction temperature. MAO (2 mL of a 10 wt.% solution in toluene) was then added to the suspension and the reaction left to stir for 20 minutes (polymer began to precipitate within

30

- 77 -

minutes). Acetone, methanol and 6M HCl were added to quench the reaction and precipitate the resulting polyethylene. The polymer was dried in a vacuum oven resulting in 400 mg of polyethylene. GPC: $M_n = 2100$; $M_w = 5600$. ^1H NMR: 30 branches/1000 carbon atoms. DSC: $T_m = 104$ C.

5

Example 57

A flame dried Fisher-Porter bottle was charged with complex D2 (5 mg, 0.0083 mmol) and 50 mL of toluene. The flask was placed in a water bath (23 C) to control reaction temperature. MAO (2 mL of a 10 wt.% solution in toluene) was then added to the suspension and the bottle rapidly pressurized to 45 psig and the reaction left to stir for 20 minutes. Acetone, methanol and 6M HCl were added to quench the reaction and precipitate the resulting polyethylene. The polymer was dried in a vacuum oven resulting in 150 mg of polyethylene. GPC: $M_w = 22,000$. ^1H NMR: 7 branches/1000 carbon atoms. DSC: $T_m = 127$ C.

10

15

Example 58

A flame dried Schlenk flask was charged with complex D4 (2 mg, 0.0036 mmol), 1 atmosphere ethylene and 50 mL of toluene. The flask was then placed in an ice-water bath (0 C) to control reaction temperature. MAO (2 mL of a 10 wt.% solution in toluene) was then added to the suspension and the reaction left to stir for 10 minutes (polymer began to precipitate within minutes). Acetone, methanol and 6M HCl were added to quench the reaction and precipitate the resulting polyethylene. The polymer was dried in a vacuum oven resulting in 560 mg of polyethylene (33,000 TO/h). GPC: $M_n = 5500$; $M_w = 27,000$. ^1H NMR: 4 branches/1000 carbon atoms. DSC: $T_m = 130$ C.

20

25

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Example 59

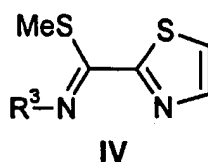
- 78 -

A flame dried Schlenk flask was charged with complex D4 (2 mg, 0.0036 mmol), 1 atmosphere ethylene and 50 mL of toluene. The flask was then placed in a water bath (23 C) to control reaction temperature. MAO (2 mL of a 10 wt.% solution in toluene) was then added to the suspension and the reaction left to stir for 10 minutes (polymer began to precipitate within minutes). Acetone, methanol and 6M HCl were added to quench the reaction and precipitate the resulting polyethylene. The polymer was dried in a vacuum oven resulting in 490 mg of polyethylene (30,000 TO/h). GPC: $M_n = 1600$; $M_w = 6100$. ^1H NMR: 20 branches/1000 carbon atoms. DSC: $T_m = 110$ C.

Ligand Synthesis

Example 60

This example illustrates the preparation of a compound IV having the formula:



for use in a catalyst system according to the third embodiment of the present invention.

2-Thiazolecarboxylic acid (0.1 mol) is reacted with 1,1-carbonyldiimidazole (0.1 mol) and 2,6-diisopropylaniline (0.1 mol) to obtain the corresponding

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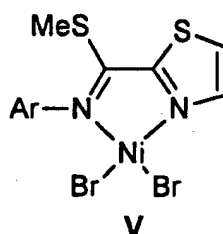
amide. This is reacted with Lawesson's reagent to form the thioamide, which is treated with MeI and base to give compound IV.

Synthesis of the Metal Complex

5

Example 61

10 This example illustrates the synthesis of a metal complex having the formula V:



15 wherein: Ar = 2,6-diisopropylphenyl.

20 A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum is charged with 0.2 mmol of compound IV from example 54 and 0.2 mmol (1,2-dimethoxyethane)nickel(II) dibromide (Aldrich) under an inert atmosphere. Dry, deoxygenated dichloromethane (5 mL) is added and the mixture is stirred under an argon atmosphere, slowly preparing a crystalline precipitate. After 1 h, another 5 mL dichloromethane is added. The mixture is stirred another 21 h at 21 C, then diluted with 10 mL dry, deoxygenated hexane and stirred another 8 h. The supernatant is removed

- 80 -

via a filter paper-tipped cannula, and the residue dried in vacuo at 1 mm Hg to afford complex V.

Olefin Polymerization

5

Example 62

10 A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum is charged with 10 mg of compound V. The flask is evacuated and refilled with ethylene, then charged with 75 mL dry, deoxygenated toluene. The resultant suspension is cooled to 0°C and allowed to equilibrate with 1 atm ethylene for 15 min, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene (Aldrich) and stirred under 1 atm
15 ethylene. After 60 minutes, the reaction is quenched by the addition of methanol, acetone and 6 N aqueous HCl to produce a polyethylene precipitate.

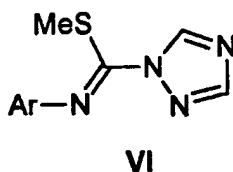
Ligand Synthesis

20

Example 63

25 This example illustrates the preparation of a compound VI having the formula:

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wherein: Ar = 2,6-diisopropylphenyl,

for use in a catalyst system according to the third embodiment of the
5 present invention.

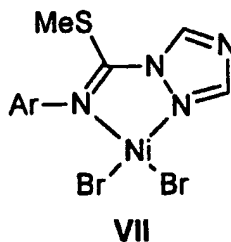
Thiophosgene (0.1 mol) is reacted with 1,2,4-triazole (0.2 mol) and
base to afford thiocarbonylditriazole. This is heated with 2,6-
diisopropylaniline (0.1 mol) to obtain the mixed thiourea, which is treated
10 with MeI (methyl-iodine) and base to give compound VI.

Synthesis of the Metal Complex

15

Example 64

This example illustrates the synthesis of a metal complex having the
formula VII:



20

wherein: Ar = 2,6-diisopropylphenyl.

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Example 65

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum is charged with 0.2 mmol of compound VI from example 57 and 0.2 mmol (1,2-dimethoxyethane)nickel(II) dibromide (Aldrich) under an inert atmosphere. Dry, deoxygenated dichloromethane (5 mL) is added and the mixture is stirred under an argon atmosphere, slowly preparing a crystalline precipitate. After 1 hour, another 5 mL dichloromethane is added. The mixture is stirred another 21 hour at 21° C, then diluted with 10 mL dry, deoxygenated hexane and stirred another 8 hour. The supernatant is removed via a filter paper-tipped cannula, and the residue dried *in vacuo* at 1 mm Hg to afford compound VII.

Olefin Polymerization

15

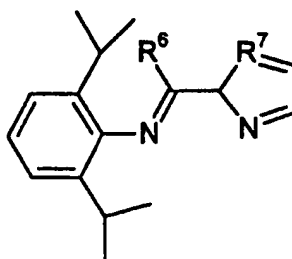
Example 66

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum is charged with 10 mg of compound VII from example 58. The flask is evacuated and refilled with ethylene, then charged with 75 mL dry, deoxygenated toluene. The resultant suspension is cooled to 0°C and allowed to equilibrate with 1 atm ethylene for 15 min, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene (Aldrich) and stirred under 1 atm ethylene. After 60 minutes, the reaction is quenched by the addition of methanol, acetone and 6 N aqueous HCl to produce a polyethylene precipitate.

Ligand Synthesis

30

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E1: $R^6 = \text{Me}$, $R^7 = \text{S}$ E2: $R^6 = \text{H}$, $R^7 = \text{N(H)}$

5

Example 67

Synthesis of E1

10 A cooled solution of 2-acetylthiazole (4 mmol) and 2,6-diisopropylaniline (12 mmol) in toluene (15 mL) is treated with TiCl_4 (2.0 mL of 1.0 M solution in toluene), immediately yielding an olive green precipitate. After allowing the reaction to warm to room temperature, stirring is continued for 72 hours before the reaction contents are filtered through

15 alumina, rinsing with ethyl acetate. The filtrate is washed sequentially with 0.6 M HCl, saturated sodium bicarbonate, and brine, then dried over magnesium sulfate, filtered, and concentrated to afford **E1** as a yellow solid.

Example 68

20

Synthesis of E2

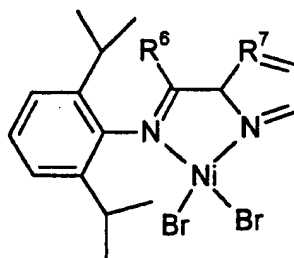
 2-Imidazolecarboxaldehyde (2.9 mmol) is added to a solution of diisopropylaniline (2.9 mmol) in ethanol (10 mL). The reaction is refluxed

25 for 4 hours, then concentrated to a small volume, taken up in ethyl acetate,

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and washed. Removal of solvent by rotary evaporation gives an oil that crystallized over time, is isolated by filtration, washed, and used without further purification.

5 Synthesis of the Metal Complex



F1: $R^6 = \text{Me}$, $R^7 = \text{S}$

F2: $R^6 = \text{H}$, $R^7 = \text{N(H)}$

10

Example 69

Synthesis of F1.

15 A molar excess of thiazole/imine **E1**, from Example 60, and
(DME)NiBr₂ are combined as solids in an inert atmospheres glove box, then
removed from the glove box and treated with dry CH₂Cl₂. The suspension
immediately develops a deep orange/brown color and is stirred overnight at
room temperature. The solvent is evaporated under a stream of argon, and
20 the precipitated solid is washed several times with hexane and
hexane/methylene chloride before being dried *in vacuo* to give the pre-
catalyst **F1** as an orange/brown powder.

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Example 70Synthesis of F2.

5 Methylene chloride (10 mL) is added to a mixture of crude
imidazole/imine E2 (100 mg), from example 61, and (DME)NiBr₂ (27 mg).
The suspension gradually develops a bright green color, then appears to
darken somewhat. After stirring overnight, the solvent is evaporated under
a stream of argon, and the precipitated solid is washed several times with
10 hexane and hexane/methylene chloride before being dried *in vacuo* to give
the pre-catalyst F2 as a yellow-green powder.

Olefin Polymerization

15

Example 71

The thiazole/imine complex F1 (12 mg), from Example 62, is
suspended in 20 mL of dry toluene. The reaction mixture is cooled to 0°C
20 and equilibrated under an ethylene atmosphere, then treated with MAO (1.8
mL of a 10 % by weight solution in toluene) and stirred under 1 atm
ethylene for 30 minutes. The reaction is quenched by the sequential
addition of acetone, methanol, and 6M HCl. The precipitated polyethylene
is isolated by filtration, washed, and dried *in vacuo*.

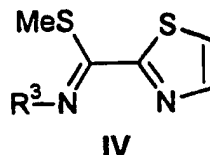
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Example 72

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Polymerization of ethylene with catalyst system IV.



5 A 500 mL round bottom flask equipped with a magnetic stir bar, and a side-arm adapter with a Kontes high vacuum valve and a 24/40 septum, is flame-dried under vacuum (0.3 mm Hg), then (in the glovebox) charged with 10.0 mg of the ligand IV, 5.0 mg Ni(1,5-cyclooctadiene)₂ (Aldrich) and 106 mg B(C₆F₅)₃ (Strem). On the Schlenk line, the flask is evacuated and
10 refilled with ethylene, then charged with 100 mL dry, deoxygenated toluene while being stirred at 21 C. After 30 min., the reaction is quenched by the addition of MeOH and acetone. The white flocculent polyethylene which separates is isolated by vacuum filtration and dried in vacuo (0.4 mm Hg, 6
15 h) to yield 5.0 g polyethylene.

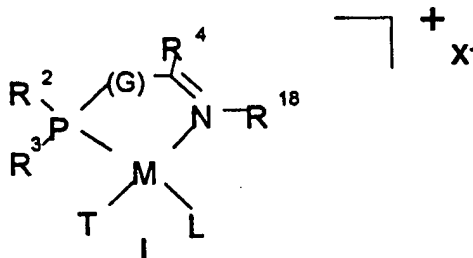
20 The invention has been described above in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications other than as specifically described herein can be effected within the spirit and scope of the invention. Moreover, all patents and literature references or other references herein are hereby incorporated by reference.

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Claims

We Claim:

1. A catalyst comprising a compound of formula I:



5 wherein:

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

10 R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^{18} is hydrocarbyl or substituted hydrocarbyl;

T is hydrogen or hydrocarbyl;

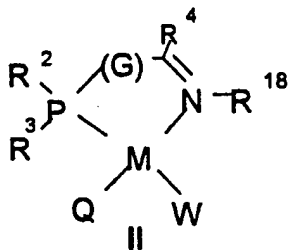
L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen, or sulfur;

15 M is Ni(II), Pd(II), or Co(II); and

X^- is a weakly coordinating anion.

2. A catalyst system wherein the catalyst is formed by contacting a first compound Y with a second compound II having the formula:

20



- 88 -

wherein:

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together
5 with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^{18} is hydrocarbyl or substituted hydrocarbyl;

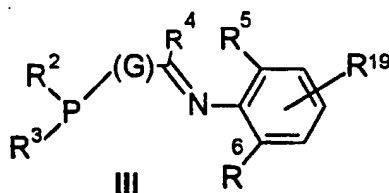
Q is hydrocarbyl, chloride, iodide or bromide;

10 W is hydrocarbyl, chloride, iodide or bromide;

M is Ni(II), Pd(II), or Co(II);

and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is
15 a weakly coordinating anion.

3. A compound of formula III:



20

wherein

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together
25 with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

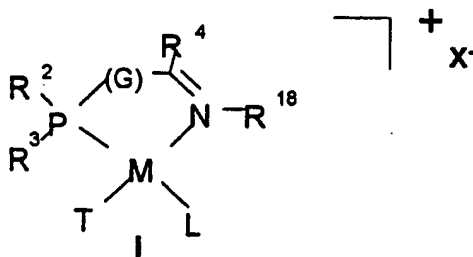
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R^{19} is hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, or nitro;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^5 and R^6 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl or halide; provided that R^5 and R^6 are not both hydrogen.

4. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst comprising a compound of formula I:



wherein:

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^{18} is hydrocarbyl or substituted hydrocarbyl;

T is hydrogen or hydrocarbyl;

L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen, or sulfur;

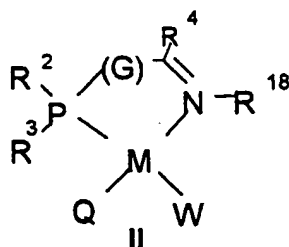
M is Ni(II), Pd(II), or Co(II); and

X^- is a weakly coordinating anion;

at a temperature and a pressure sufficient to effect polymerization.

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5. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst system wherein the catalyst is formed by contacting a first compound Y with a second compound II having the formula:



10 wherein:

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together with phosphorus to form a ring;

G is hydrocarbyl or substituted hydrocarbyl;

15 R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^{18} is hydrocarbyl or substituted hydrocarbyl;

Q is hydrocarbyl, chloride, iodide or bromide;

W is hydrocarbyl, chloride, iodide or bromide;

M is Ni(II), Pd(II), or Co(II);

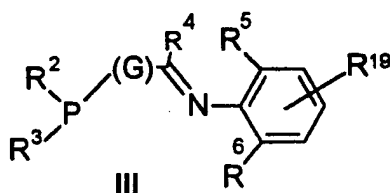
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and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

25

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6. A process for the polymerization of olefins comprising contacting a compound of the formula III with a suitable nickel precursor, optionally a Lewis or Bronsted acid and one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin:



wherein

10

R^2 and R^3 are each independently selected from hydrocarbyl, or substituted hydrocarbyl, and in addition, R^2 and R^3 may be taken together with phosphorus to form a ring;

15 G is hydrocarbyl or substituted hydrocarbyl and may comprise a cyclic olefin;

R^{19} is hydrogen, hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, or nitro;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl; and

20 R^5 and R^6 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl or halide; provided that R^5 and R^6 are not both hydrogen.

7. The process of claim 4 where the monomer of the formula $R'CH=CHR''$ is ethylene.

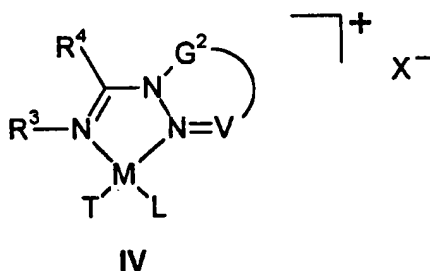
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8. The process of claim 5 where the monomer of the formula $R'CH=CHR''$ is ethylene.

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9. The process of claim 6 where the monomer of the formula $R'CH=CHR''$ is ethylene.

5 10. A catalyst comprising a compound of formula IV:



10

wherein:

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

15 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

V is CR^6 , N, or PR^6R^9 ;

20 R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

25 L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur;

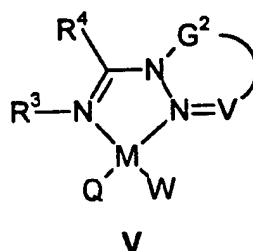
M is Ni(II), Pd(II), or Co(II); and

- 93 -

X⁻ is a weakly coordinating anion.

11. A catalyst system wherein the catalyst is formed by contacting a first compound Y with a second compound V having the formula:

5



wherein:

10

R³ is hydrocarbyl or substituted hydrocarbyl;

R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

G² is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G², V, N, and N;

15

V is CR⁶, N, or PR⁶R⁹;

R⁶ and R⁹ are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R⁶ and R⁹ may collectively form a ring with phosphorus;

20

Q is hydrocarbyl, chloride, iodide, or bromide;

W is hydrocarbyl, chloride, iodide, or bromide;

M is Ni(II), Pd(II), or Co(II);

and Y is a neutral Lewis acid capable of abstracting Q⁻ or W⁻ to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a

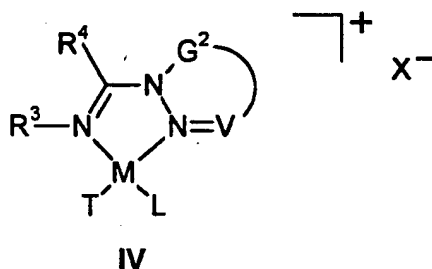
25

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weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

12. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst comprising a compound of formula IV:

10



15 wherein:

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

V is CR^6 , N, or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

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L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur;

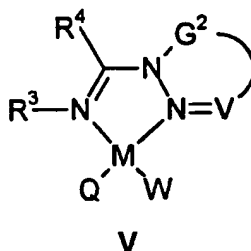
M is Ni(II), Pd(II), or Co(II);

and X⁻ is a weakly coordinating anion.

5

13. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula R'¹CH=CHR'' wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst wherein the catalyst is formed by contacting a first compound Y with a second compound V having the formula:

10



15

wherein:

R³ is hydrocarbyl or substituted hydrocarbyl;

R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

20

G² is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G², V, N, and N;

V is CR⁶, N, or PR⁶R⁹;

R⁶ and R⁹ are each independently selected from hydrogen,

25

hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected

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hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

Q is hydrocarbyl, chloride, iodide, or bromide;

W is hydrocarbyl, chloride, iodide, or bromide;

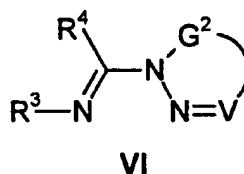
5 M is Ni(II), Pd(II), or Co(II);

and Y is a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

10

14. A process for the polymerization of olefins comprising contacting a compound of the formula VI with a suitable nickel precursor, optionally a Lewis or Bronsted acid and one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin:

15



20

wherein:

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

25

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

V is CR^6 , N, or PR^6R^9 ;

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R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus.

5

15. The process of claim 12 where the monomer of the formula $R'CH=CHR''$ is ethylene.

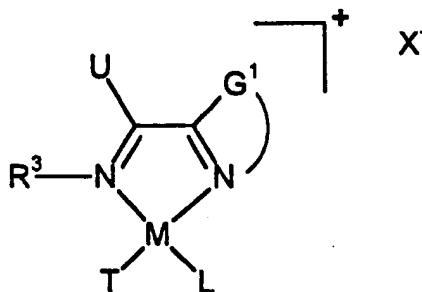
16. The process of claim 13 where the monomer of the formula
10 $R'CH=CHR''$ is ethylene.

17. The process of claim 14 where the monomer of the formula $R'CH=CHR''$ is ethylene.

15 18. A catalyst comprising a compound of the formula VII:

20

25



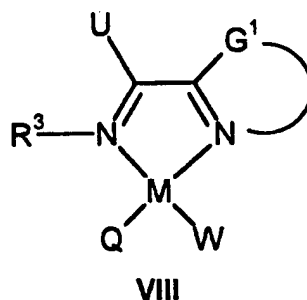
VII

- 98 -

wherein:

- 5 R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;
 U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;
 R^4 and R^8 are each independently selected from hydrogen,
 hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may
 collectively form a ring with nitrogen;
 10 G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a
 carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-
 membered heterocyclic ring comprising G^1 , C, and N;
 T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;
 L is a monoolefin or a neutral Lewis base where the donating atom is
 15 nitrogen, oxygen or sulfur;
 M is $Ni(II)$, $Pd(II)$, or $Co(II)$; and
 X^- is a weakly coordinating anion.

19. A catalyst system wherein the catalyst is formed by contacting
 20 a first compound Y with a second compound VIII having the formula:



25 wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

- 99 -

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

5 G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1 , C, and N;

M is Ni(II), Pd(II), or Co(II);

Q is hydrocarbyl, chloride, iodide, or bromide;

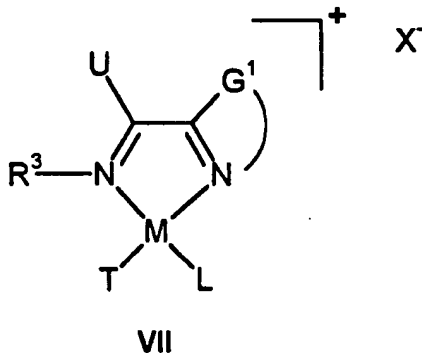
10 W is hydrocarbyl, chloride, iodide, or bromide;

and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

15

20. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst comprising a compound of the

20 formula VII:



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wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

5 R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1 , C, and N;

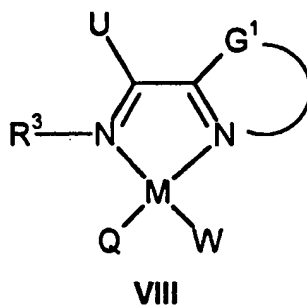
T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur;

M is Ni(II), Pd(II), or Co(II); and

15 X^- is a weakly coordinating anion.

21. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be
20 linked to form a cyclic olefin; with a catalyst system wherein the catalyst is formed by contacting a first compound Y with a second compound VIII having the formula:



- 101 -

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

5 R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-
10 membered heterocyclic ring comprising G^1 , C, and N;

M is Ni(II), Pd(II), or Co(II);

Q is an hydrocarbyl, chloride, iodide, or bromide;

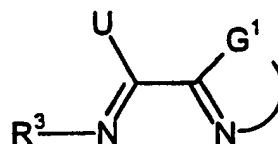
W is hydrocarbyl, chloride, iodide, or bromide;

and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^-
15 to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

22. The process as described in claim 21 where the Lewis acid is
20 MAO.

23. A process for the polymerization of olefins comprising
contacting a compound of the formula IX with a suitable nickel precursor,
optionally a Lewis or Bronsted acid and one or more olefin monomers of the
25 formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin:

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IX

wherein:

R³ is hydrocarbyl, substituted hydrocarbyl or silyl;

5 U is OR⁴, SR⁴, SeR⁴ or NR⁴R⁸;

R⁴ and R⁸ are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R⁴ and R⁸ may collectively form a ring with nitrogen;

10 G¹ is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G¹, C, and N.

24. The process of claim 20 where the monomer is ethylene.

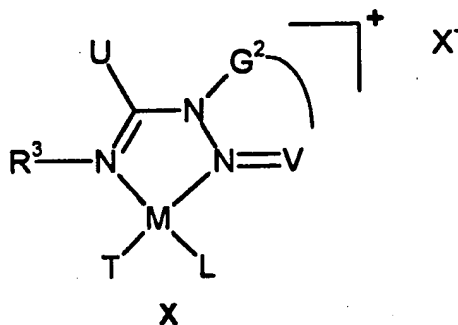
15 25. The process of claim 21 where the monomer is ethylene.

26. The process of claim 23 where the monomer is ethylene.

27. A catalyst comprising the formula X:

20

- 103 -

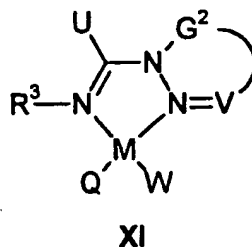


wherein:

- 5 R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;
 U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;
 R^4 and R^8 are each independently selected from hydrogen,
 hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may
 collectively form a ring with nitrogen;
- 10 V is CR^6 , N , or PR^6R^9 ;
 R^6 and R^9 are each independently selected from hydrogen,
 hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected
 hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with
 phosphorus;
- 15 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a
 carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-
 membered heterocyclic ring comprising G^2 , V , N , and N ;
 T is hydrogen, hydrocarbyl, or a substituted hydrocarbyl;
 L is a monoolefin or a neutral Lewis base where the donating atom is
- 20 nitrogen, oxygen, sulfur;
 M is $Ni(II)$, $Pd(II)$, $Co(II)$; and
 X^- is a weakly coordinating anion.

- 25 28. A catalyst system wherein the catalyst is formed by contacting a
 first compound Y with a second compound XI having the formula:

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5

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

10 U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

V is CR^6 , N , or PR^6R^9 ;

15 R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

20 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V , N , and N ;

M is $Ni(II)$, $Pd(II)$, or $Co(II)$;

Q is hydrocarbyl, chloride, iodide, or bromide;

W is hydrocarbyl, chloride, iodide, or bromide;

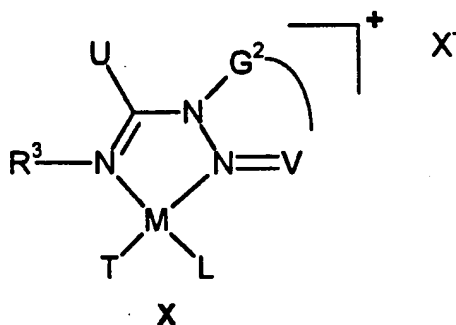
25 and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion

- 105 -

is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

- 5 29. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst comprising the formula X :

10



wherein:

15

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

20

V is CR^6 , N , or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

25

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G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

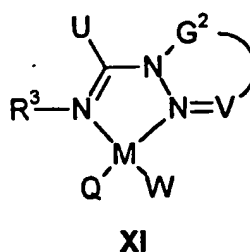
T is hydrogen, hydrocarbyl, or a substituted hydrocarbyl;

5 L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen, sulfur;

M is Ni(II), Pd(II), Co(II); and

X^- is a weakly coordinating anion.

10 30. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin; with a catalyst wherein the catalyst is formed by contacting a first compound Y with a second compound XI having the
15 formula:



20

wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

25 U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

- 107 -

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

V is CR^6 , N, or PR^6R^8 ;

5 R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

10 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

M is Ni(II), Pd(II), or Co(II);

Q is hydrocarbyl, chloride, iodide, or bromide;

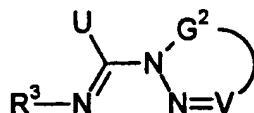
W is hydrocarbyl, chloride, iodide, or bromide;

15 and Y is selected from a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion.

20 31. The process as described in claim 30 where the Lewis acid is MAO.

25 32. A process for the polymerization of olefins comprising contacting a compound of the formula XII with a suitable nickel precursor, optionally a Lewis or Bronsted acid and one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be linked to form a cyclic olefin:

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XII

5 wherein:

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen,
hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may
10 collectively form a ring with nitrogen;

V is CR^6 , N, or PR^6R^9 ;

R^6 and R^9 are each independently selected from hydrogen,
hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected
hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with
15 phosphorus;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a
carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-
membered heterocyclic ring comprising G^2 , V, N, and N.

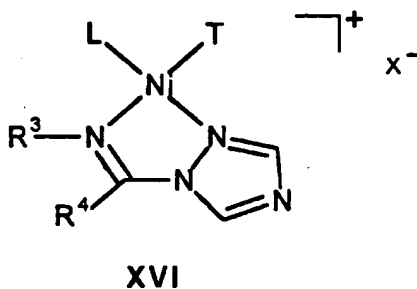
20 33. The process of claim 29 where the monomer of the formula
 $R'CH=CHR''$ is ethylene.

34. The process of claim 30 where the monomer of the formula
 $R'CH=CHR''$ is ethylene.

25 35. The process of claim 32 where the monomer of the formula
 $R'CH=CHR''$ is ethylene.

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36. A catalyst comprising the formula **XVI**:



wherein:

5

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

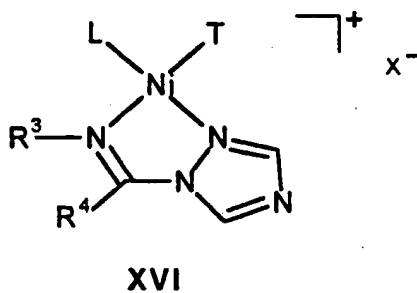
L is a monoolefin or a neutral Lewis base where the donating
atom is nitrogen, oxygen or sulfur; and

10

X is a weakly coordinating anion.

37. A process for preparing polyolefins comprising contacting one or
more olefin monomers having the composition $R'CH=CHR''$ wherein R' and
 R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may
be linked to form a cyclic olefin; with a catalyst comprising the formula **XVI**:

15



20

- 110 -

wherein:

R^3 is hydrocarbyl or substituted hydrocarbyl;

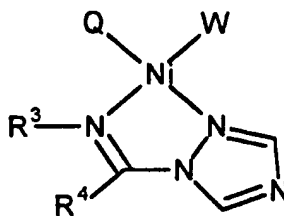
R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

5 T is hydrogen, hydrocarbyl, or substituted hydrocarbyl;

L is a monoolefin or a neutral Lewis base where the donating atom is nitrogen, oxygen or sulfur; and

X^- is a weakly coordinating anion.

10 38. A catalyst system comprising a compound of the formula **XVII**:



XVII

wherein:

15

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

Q is hydrocarbyl, chloride, iodide, or bromide;

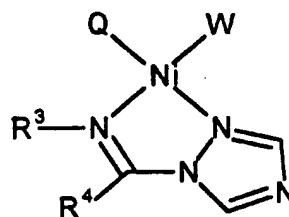
W is hydrocarbyl, chloride, iodide, or bromide.

20

39. A process for preparing polyolefins comprising contacting one or more olefin monomers of the formula $R'CH=CHR''$ wherein R' and R'' are independently hydrogen, hydrocarbyl, fluoroalkyl, or R' and R'' may be

- 111 -

linked to form a cyclic olefin; with a catalyst system comprising a compound of the formula **XVII**:

**XVII**

5

wherein:

R³ is hydrocarbyl or substituted hydrocarbyl;

R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

10 Q is hydrocarbyl, chloride, iodide, or bromide; and

W is hydrocarbyl, chloride, iodide, or bromide.

40. A process for the polymerization of olefins comprising contacting one or more monomers of the formula R'CH=CHR'' with a binucleating or multinucleating ligand complexed to a Group 8-10 transition metal M and one or more Lewis acids, wherein the Lewis acid or acids are bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to the transition metal M; and R' and R'' are each, independently selected from hydrogen, hydrocarbyl, fluoroalkyl, or may be linked to form a cyclic olefin.

20

41. The process of Claim 40 wherein the metal is nickel.

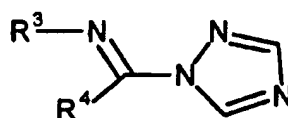
42. The process of Claim 41 wherein the Lewis acid is a boron or aluminum containing Lewis acid.

25

- 112 -

43. A composition comprising (i) a Group 8-10 transition metal M,
(ii) one or more Lewis acids, and (iii) a binucleating or multinucleating
compound of the formula XVIII:

5



XVIII

wherein the Lewis acid or acids are bound to one or more heteroatoms
which are π -conjugated to the donor atom or atoms bound to the transition
metal M;

10

R³ is hydrocarbyl or substituted hydrocarbyl;

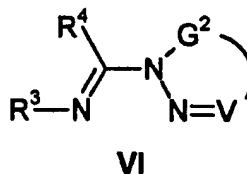
R⁴ is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl.

44. The composition of Claim 43 wherein the transition metal M is
Ni(II), and the Lewis acid is a boron or aluminum containing Lewis acid.

15

45. A composition comprising (i) a Group 8-10 transition metal M,
(ii) one or more Lewis acids, and (iii) a binucleating or multinucleating
compound of the formula VI:

20



VI

- 113 -

wherein the Lewis acid or acids are bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to the transition metal M;

R^3 is hydrocarbyl or substituted hydrocarbyl;

5 R^4 is hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl;

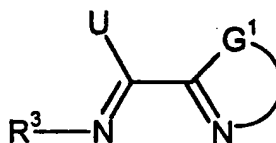
G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N;

V is CR^6 , N, or PR^6R^9 ;

10 R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus.

15 46. The composition of Claim 45 wherein the transition metal M is Ni(II), and the Lewis acid is a boron or aluminum containing Lewis acid.

20 47. A composition comprising (i) a Group 8-10 transition metal M, (ii) one or more Lewis acids, and (iii) a binucleating or multinucleating compound of the formula IX:



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wherein the Lewis acid or acids are bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to a transition metal M;

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

5 U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

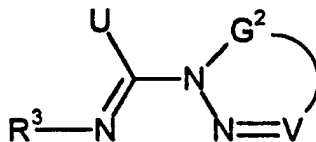
10 G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1 , C, and N.

48. The composition of Claim 47 wherein the transition metal M is Ni(II), and the Lewis acid is a boron or aluminum containing Lewis acid.

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49. A composition comprising (i) a Group 8-10 transition metal M, (ii) one or more Lewis acids, and (iii) a binucleating or multinucleating compound of the formula XII:

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XII

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wherein the Lewis acid or acids are bound to one or more heteroatoms which are π -conjugated to the donor atom or atoms bound to a transition metal M;

R^3 is hydrocarbyl, substituted hydrocarbyl or silyl;

5 U is OR^4 , SR^4 , SeR^4 or NR^4R^8 ;

R^4 and R^8 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, and in addition, R^4 and R^8 may collectively form a ring with nitrogen;

V is CR^6 , N, or PR^6R^9 ;

10 R^6 and R^9 are each independently selected from hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

15 G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2 , V, N, and N.

50. The composition of Claim 49 wherein the transition metal M is Ni(II), and the Lewis acid is a boron or aluminum containing Lewis acid.

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51. The catalyst of claim 1 or 2 where M is Ni(II).

52. The process of claim 4 or 5 where M is Ni(II).

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53. The catalyst of claim 10 or 11 where M is Ni(II).

54. The process of claim 12 or 13 where M is Ni(II).

55. The process of claim 20 or 21 where M is Ni(II).

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56. The process of claim 29 or 30 where M is Ni(II).

57. The catalyst of claim 18 or 19 where M is Ni(II).

5 58. The catalyst of claim 27 or 28 where M is Ni(II).

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 31/18, C08F 4/70, C07F 9/50, 15/00, 15/04, 15/06, C08F 10/00		A3	(11) International Publication Number: WO 98/40420 (43) International Publication Date: 17 September 1998 (17.09.98)																		
(21) International Application Number: PCT/US98/03592 (22) International Filing Date: 24 February 1998 (24.02.98)		(81) Designated States: CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).																			
(30) Priority Data: <table border="0"><tr><td>60/040,754</td><td>13 March 1997 (13.03.97)</td><td>US</td></tr><tr><td>60/044,691</td><td>18 April 1997 (18.04.97)</td><td>US</td></tr><tr><td>60/045,337</td><td>1 May 1997 (01.05.97)</td><td>US</td></tr><tr><td>60/045,357</td><td>2 May 1997 (02.05.97)</td><td>US</td></tr><tr><td>60/045,358</td><td>2 May 1997 (02.05.97)</td><td>US</td></tr><tr><td>60/045,697</td><td>6 May 1997 (06.05.97)</td><td>US</td></tr></table>		60/040,754	13 March 1997 (13.03.97)	US	60/044,691	18 April 1997 (18.04.97)	US	60/045,337	1 May 1997 (01.05.97)	US	60/045,357	2 May 1997 (02.05.97)	US	60/045,358	2 May 1997 (02.05.97)	US	60/045,697	6 May 1997 (06.05.97)	US	Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
60/040,754	13 March 1997 (13.03.97)	US																			
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(71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).		(88) Date of publication of the international search report: 11 February 1999 (11.02.99)																			
(72) Inventors: KILLIAN, Christopher, Moore; 1201 Hillendale Road, Gray, TN 37615 (US). MCDEVITT, Jason, Patrick; 3651 Sleepy Hollow Road, Wake Forest, NC 27587 (US). MACKENZIE, Peter, Borden; 1040 Sussex Drive, Kingsport, TN 37660 (US). MOODY, Leslie, Shane; 3322 Pine Timbers Drive, Johnson City, TN 37604 (US). PONASIK, James, Allen, Jr.; 2601 John B. Dennis Highway #1410, Kingsport, TN 37660 (US).																					
(74) Agent: GRAVES, Bernard, J., Jr.; P.O. Box 511, Kingsport, TN 37662-5075 (US).																					
(54) Title: CATALYST COMPOSITIONS FOR THE POLYMERIZATION OF OLEFINS																					
(57) Abstract <p>The present invention includes novel ligands which may be utilized as part of a catalyst system. A catalyst system of the present invention is a transition metal-ligand complex. In particular, the catalyst system includes a transition metal component and a ligand component comprising a Nitrogen atom and/or functional groups comprising a Nitrogen atom, generally in the form of an imine functional group. In certain embodiments, the ligand component may further comprise a phosphorous atom. Preferred ligand components are bidentate (bind to the transition metal at two or more sites) and include a nitrogen-transition metal bond. The transition metal-ligand complex is generally cationic and associated with a weakly coordinating anion. A catalyst system of the present invention may further comprise a Lewis or Bronsted acid. The Lewis or Bronsted acid may be complexed with the ligand component of the transition metal-ligand complex.</p>																					

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/03592

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J31/18 C08F4/70 C07F9/50 C07F15/00 C07F15/04
C07F15/06 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C07F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>WEHMAN P ET AL: "Influence of various P/N and P/P ligands on the palladium-catalysed reductive carbonylation of nitrobenzene"</p> <p>JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 535, no. 1-2, 15 May 1997, page 183-193 XP004082178</p> <p>see page 184, column 2</p> <p>see page 191 (P/N-4)</p> <p>see page 192, column 1, paragraph 1</p> <p style="text-align: center;">--- -/--</p>	3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 November 1998

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/03592

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	SHIRAKAWA E ET AL: "On the Catalytic Cycle of the Palladium-Catalyzed Cross-Coupling Reaction of Alkynylstannane with Aryl Iodide" TETRAHEDRON LETTERS, vol. 38, no. 29, 21 July 1997, page 5177-5180 XP004082975 see the whole document ---	1,2,4,5, 7,8
Y	JOHNSON L K ET AL: "MEW PD(II)- AND NI(II)-BASED CATALYSTS FOR POLYMERIZATION OF ETHYLENE AND ALPHA-OLEFINS" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 117, no. 23, 14 June 1995, page 6414/6415 XP002025459 cited in the application see the whole document ---	1,2,4,5, 7,8
P,X	VAN DEN BEUKEN, ESTHER K. ET AL: "Oligomerization of ethene by new palladium iminophosphine catalysts" CHEM. COMMUN. (CAMBRIDGE) (1998), (2), 223-224 CODEN: CHCOFS;ISSN: 1359-7345, XP002066973 see the whole document ---	1-5,7,8
Y	WO 97 02298 A (DU PONT ;JOHNSON LYNDA KAYE (US); FELDMAN JERALD (US); KREUTZER KR) 23 January 1997 see examples 130,131 ---	18-26
P,Y	WO 98 03521 A (BEEK JOHANNES A M VAN ;TURNER HOWARD (US); BOUSSIE THOMAS (US); GO) 29 January 1998 see page 66; example 5 ---	18-26
A	JIANG, ZHAOZHONG ET AL: "Stereo- and Enantioselective Alternating Copolymerization of.alpha.-Olefins with Carbon Monoxide. Synthesis of Chiral Polymers" MACROMOLECULES (1994), 27(10), 2694-700 CODEN: MAMOBX;ISSN: 0024-9297, XP000445666 see abstract see page 2695, column 2, paragraph 2 - page 2696, column 2, paragraph 3 ---	18-26
P,X	WO 97 47661 A (UNIV WARWICK ;HADDLETON DAVID MARK (GB)) 18 December 1997 see claims 3,7,8 ---	23
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/03592

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HVASTIJOVA, M. ET AL: "Structure properties of dicyanamide and tricyanmethanide complexes of copper(II), nickel(II) and cobalt(II) with ligands of pyrazole type - nucleophilic addition in the studied systems" PROC. CONF. COORD. CHEM. (1987), 11TH, 109-14 CODEN: PCCHDB; ISSN: 0139-9535, XP002085229	49
A	EP 0 748 821 A (HOECHST AG) 18 December 1996 see claims 1,10,12,15 see example 1	40

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 98/03592

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-9,51,52

Claims 1-9,51,52: Compound of formula III, catalyst containing a metallic complex I or II (containing the structure of III), process for the polymerisation of olefin with I,II or with the reaction product of III with a Nickel precursor.

The special technical feature linking this group of claims is the structure III.

2. Claims: 10-17,45,46,53,54

Catalyst comprising a compound of formula IV (including the structure of compound VI) or a precursor thereof, olefin polymerisation process therewith and composition comprising compound VI, a transition metal and a Lewis acid.

The technical feature linking this group of claims is the structure VI.

3. Claims: 18-26,47,48,55,57

Catalyst comprising a compound of formula VII (including the structure of compound IX) or one of its precursor, olefin polymerisation therewith and composition containing a compound IX, a transition metal and a Lewis acid.

The technical feature linking this group of claims is the structure IX.

4. Claims: 27-35,49,50,56,58

Catalyst containing a metallic complex of formula X (containing the structure XII) or its precursor, olefin polymerisation process therewith and composition comprising the compound XII, a transition metal and a Lewis acid.

The technical feature linking this group of claims is the structure XII.

5. Claims: 36-39,43,44

Catalyst comprising a compound of formul XVI (containing the structure XVIII) or its precursor, and composition comprising a compound XVIII, a transition metal and a Lewis acid.

The technical feature linking this group of claims is the structure XVIII.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

6. Claims: 40-42

Claims 40-42: Process for the polymerisation of olefins with a binucleating or multinucleating ligand complexed to a transition metal and a Lewis acid wherein the Lewis acid is bound to one heteroatom which is π -conjugated to the atom bound to the transition metal.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/03592

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